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Water Treatment

WATER TREATMENT

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ВОДОПОДГОТОВКА

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Contents

Introduction

0.1. General •

The use of water in steam boiler units is associated with a number of difficulties arising for the most part because water contains substances capable of disturbing normal operation of a boiler unit and turbine. Water is often responsible for the formation of deposits on the water-side heating surfaces of boiler units, and since these deposits possess low thermal conductivity, they cause overheating of tubes, thereby reducing the strength of metal. Due to a number of reasons, a certain amount of impurities contained in boiler water passes into the steam generated in the boiler unit; individual impurities, silicic acid, for instance, are apt to go from the water into the steam in greater quantities than other substances.

Impurities carried over from the boiler unit fall out of the steam which flows through the steam-generating circuit, in the form of various solid compounds. They sometimes form considerable deposits in steam superheaters, on blades and in nozzles of steam turbines and disturb the performance of power units. That is why it is vitally important to prevent the carry-over of impurities with steam or to reduce it to some admissible minimum.

In various sections of the steam-generating circuit metal is exposed to water of different composition. Water or steam sometimes acquires aggressive properties along individual sections and attacks and destroys the metal. This process, referred to as corrosion, can impair the operating conditions of heat-power equipment. Reliable operation of electric power stations thus presupposes prevention of not only scale or salts deposition, but also corrosion damage.

Of much importance to the elimination of the above mentioned demerits is suitable treatment, or conditioning, of water and condensate supplied into the feedwater system of a boiler unit. Such water treatment includes various technological processes, such as

clarification, softening, demineralization, desilication, degasification, etc.

Thus, the ultimate aim of water treatment is to ensure an efficient and reliable water conditioning cycle at electric power stations by introducing suitable water-treatment methods and properly organizing internal boiler-water processes. Water-treatment practice makes wide use of the theoretical principles, conclusions and achievements of physics, thermodynamics and chemistry. In this respect, the knowledge of chemistry is of crucial importance in understanding the essence of the many processes involved in water treatment.

0.2.   Basic Concepts and Definitions

The steam-water cycle of modern power stations is characterized by the presence of various steam-, water- and condensate flows that affect the quality of feedwater for boiler units.

The water drawn from the water-supply source of a power plant is called *initial* (sometimes *raw*, *non-treated*). The quality of raw water is usually improved through special treatment. The plants in which raw water undergoes such treatment are known as *water-treatment plants*, and the water obtained is referred to as *chemically treated water*. Water supplied to boiler units is called *feedwater*, and water contained in boiler units is known as *boiler water*.

Shown in Fig. 0.1 is the basic flow diagram of a modern supercritical-pressure (25.5 MPa) boiler-turbine unit rated 300 MW. The steam generated in boiler unit *1* is directed through superheater *2* into a steam turbine consisting of superhigh-pressure cylinder (SHPC) *3*, high-pressure cylinder (HPC) *4*, intermediate-pressure cylinder (IPC) *5*, and low-pressure cylinder (LPC) *6*. The superheated steam generated in the boiler unit is referred to as *main steam*. First, it flows in succession through the SHPC and the HPC and then through steam reheater *7*, in which the steam temperature is raised from 593 to 838 K. Further, the steam at that temperature and a pressure of 3.6 MPa is directed into the IPC and LPC and then into condenser *8*, where it is cooled by water called the *cooling* or *circulating water*. The steam condenses in the condenser forming what is known as *turbine condensate*.

First-stage condensate pumps *9* deliver the turbine condensate to demineralizing plant *10* where it is freed of suspended and ionized impurities. Second-stage condensate pumps *11* deliver the

Fig. 0.1. Basic flow diagram of a modern supercritical-pressure boiler-turbine unit rated 300 MW

demineralized condensate through low-pressure regenerative feedwater heaters *12* into deaerator *14* to which heater condensate flows from the high-pressure regenerative feedwater heaters.
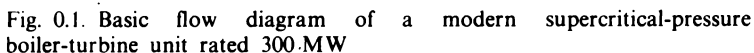
Since not only turbine condensate, but also other kinds of condensate are treated in the deaerator, the mixture leaving it is already called *feedwater* (and also *deaerated water*). After being heated in the deaerator by steam *17* to 428 K and properly degasified (i.e. freed from the dissolved gases, O_2, CO_2, N_2), feedwater flows from the deaerator to booster boiler feed pumps *15*, which deliver it to the suction line of feed pumps *16*. The latter direct the feedwater through high-pressure heater *18* into boiler unit *1* where the above described steam-water cycle closes.

For supercritical-pressure boiler-turbine units the losses of steam and condensate fall within 1 to 2 per cent of boiler unit capacity; they are made up for by *demineralized water* (referred to as *make-up water*) treated in a special water-treatment plant *13*.

Figure 0.2 depicts the flow diagram of a heat and electric power station, or plant. Superheated steam *2* generated in boiler unit *1* is directed to turbine *3*, from which exhaust steam passes into

condenser *4* where the steam condenses. Pump *5* delivers the turbine condensate, via low-pressure regenerative feedwater heaters *6*, to deaerator *7*, to which chemically treated water and other kinds of condensate are also delivered. Then, feedwater pump *8* directs the deaerated water to the boiler unit via high-pressure regenerative feedwater heaters *9*.
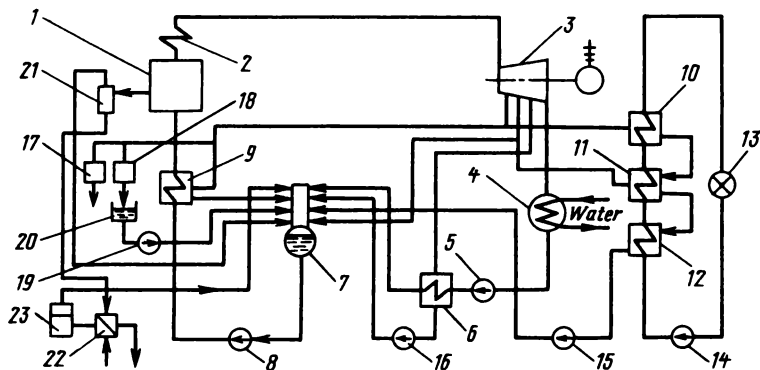
Fig. 0.2. Flow diagram of a heat and electric power station

In addition to electric power, a heat and electric power station produces and delivers to consumers hot water and steam. Hot water for outside consumers is prepared in heat-distribution system heaters or boilers *10-12*, in which water is heated by steam taken from turbine extraction points to the required temperature. Cooled water is returned from consumers *13* by heat-distribution system pump *14* and delivered again to boilers *10-12*. The condensate formed in boilers and in low-pressure heaters is delivered by condensate pumps *15* and *16* into deaerator *7*. Steam supplied for processing purposes is utilized by consumers *17* and *18*. The possibility of repeated usage of industrial condensate in the boiler units of a heat and electric power plant depends on how the steam is being used and for what purposes. In the flow diagram investigated, industrial condensate is returned from consumers *18*, while no condensate is returned from consumer *17*.

The industrial condensate whose qualities meet the adopted standards is delivered into the deaerator by pump *19* mounted

downstream from condensate return tank *20*. Otherwise, the returned industrial condensate is delivered into a water-treatment plant for oil removal, softening, desilication, deferrization, etc.

Heat and electric power plants are usually fitted with natural-circulation drum-type steam generators. A small fraction of the boiler water is withdrawn from these boiler units into flash tank *21* and then discharged, through heat exchanger *22*, into the sewerage (drain). This rejected water is referred to as *blowdown water*. It can be used, for instance, as makeup water for heat-distribution systems and for other purposes. Blowdown water is usually cooled by the raw water delivered into the water-treatment plant. The steam produced in flash tank *23* is usually directed into the deaerator.

0.3. Steam-Water Balance of a Heat and Electric Power Plant

Having considered the basic flow diagram of a heat and electric power plant, we can single out the following flows that pass into the feedwater system of boiler units: turbine condensate, condensate from heat-distribution system heaters, condensate from regenerative feedwater heaters, industrial condensate, and chemically treated water from the water-treatment plant.

There are always losses of condensate and water in the water-steam cycle of a station and outside the cycle. These losses include station losses L_s, processing losses L_p and the loss associated with boiler blowdown water L_b. The total losses

$$L_t = L_s + L_p + L_b \tag{0.1}$$

are usually expressed as a percentage of the quantity of feedwater. The losses L_s and L_p are also expressed in per cent of the total steam capacity of boiler units. The water added into the feedwater system of boiler units, Q_m, to make up for the losses in steam, condensate and water, is known as *makeup water* or simply makeup; it is usually expressed in per cent of the quantity of feedwater D_{fw}

$$\alpha_m = \frac{Q_m}{D_{fw}} 100 \tag{0.2}$$

Chemically treated water Q_{ch} and distillate Q_{dt} (the condensate of condenser vapour or secondary steam) can be used as makeup water,

i. e.

$$Q_m = Q_{ch} + Q_{dt} \tag{0.3}$$

However, chemically treated water is most often used as makeup water. The ratio

$$\alpha_{ch} = \frac{Q_{ch}}{D_{fw}} \, 100 \tag{0.4}$$

is called chemically treated makeup.

If chemically treated water contains S_{ch} milligrams of various substances per litre, then the amount of these substances introduced into feedwater is

$$\Delta S_{fw} = \frac{\alpha_{ch}}{100} \, S_{ch} \tag{0.5}$$

The measure of water control practiced in operating boiler units is characterized by the quantity ΔS_{fw}. The attending personnel of an electric power station at which the value of ΔS_{ch} is greater than that at other stations must pay more attention to and make greater efforts in controlling water conditions. This quantity can be referred to as *salt addition*. In practice, the tendency is to reduce ΔS_{ch} to a minimum, which can be done by diminishing α_{ch} or S_{ch}. To decrease α_{ch}, it is necessary to minimize the total losses of steam, condensate and water. The quantity S_{ch} can be decreased by removing substances dissolved in water, i. e. by subjecting the water to special treatment, known as *demineralization*. There is also a third way of dealing with the problem, where the process permits of high salt additions (multistage evaporation).

Condensate is the most valuable component of feedwater because it contains rather small amounts of dissolved substances. Possible deterioration of the quality of condensate must however be taken into account. Sometimes, due to the considerable contamination of returned industrial condensate (with iron, petroleum products), it becomes economically advantageous to discharge the return condensate into the sewerage and replace it by chemically treated water. One ton of lost condensate is replaced by

$$q_{ch} = \frac{1}{1 - \dfrac{S_{ch}}{S_{bw}}(1 - \beta)}$$

tons of chemically treated water. When $S_{ch} \to 0$, which is equivalent to the use of distillate to make up for the loss, $q_{ch} \to 1$; at $S_{ch} \to \to S_{bw}$, the value of q_{ch} increases substantially and at $\beta \to 0$ it tends to infinity, which must be borne in mind when determining the capacity of the water treatment plant. Here S_{ch} and S_{bw} represent the concentration of a substance (used for calculation of salt content, alkalinity, etc.) in chemically treated and boiler water; β is the fraction of steam separated in the continuous-blowdown flash tank.

The total amount of feedwater for steam boiler units, D_{fw} (m³/h), is determined by the equality

$$D_{fw} = Q_m + Q_c = Q_{ch} + Q_{dt} + Q_c$$

where Q_c is the total amount of condensate returned into boiler units with feedwater.

The loss of water due to blowdown of boiler units, m³/h,

$$L_{bd} = p_s D_s \cdot 10^{-2} (1 - \beta)$$

where p_s and D_s are the blowdown water and steam capacity of a boiler unit, respectively (see Sec. 4.5).

At modern electric power stations fitted with boiler-turbine units the loss of steam and condensate, L_s, does not exceed 2 per cent and falls within 0.5-1.0 per cent when proper attendance is ensured. The loss L_s at conventional electric power stations may reach 3 to 4 per cent, but these losses may be cut down to 1-1.5 per cent by practicing proper operating conditions and thorough control of losses.

The loss of processing steam and condensate L_p depends on the kind of industrial enterprises, the degree of perfection with which condensate is collected at the enterprise and on other conditions. This loss ranges from 40-50 to 80-100 per cent.

Chapter 1

Aqueous Solutions and Their Properties

1.1. Ways of Expressing the Concentration of Solutions

The amount of substance contained in a definite space or in a definite mass of a solution or solvent is referred to as the concentration of the solution or as the concentration of the given substance in the solution.

In water-treatment practice, the concentration of solutions is usually expressed in mass (weight) per cent, through volume concentration, number of gram-molecules (molar concentration) or gram-equivalents (normal or equivalent concentration) per litre of solution. The number of mass parts of a substance per 100 mass parts of a solution gives the percentage concentration of the solution, C_{mp}:

$$C_{mp} = \frac{g \cdot 100}{10^3 V_s \rho_s} \qquad (1.1)$$

where V_s = volume of solution, l

g = mass of substance dissolved in the volume, g

ρ_s = denstiy of solution, kg/l

This method of expressing concentration is mainly used to define the concentration of reagents applied in water-treatment plants.

Volume concentration C_{vc} is expressed in milligrams (grams, kilograms) of a substance present in a unit volume (litre, cubic meter):

$$C_{vc} = \frac{g}{V_s} \qquad (1.2)$$

Molar concentration C_m indicates the number of gram-molecules

of a given substance dissolved in 1 litre of solution:

$$C_m = \frac{C_{vc}}{M} = \frac{g}{V_s M}$$ (1.3)

where M is the molecular mass of substance.

In water-treatment practice, concentration is most commonly expressed through the number of equivalents of a substance present in 1 litre of solution. The equivalent mass (weight) of a given substance is the quantity of the substance that will combine with or replace in a given reaction one atom of hydrogen (or another monovalent element), or the amount of the substance corresponding to the transition of one electron (in oxidizing-reducing reactions). By milligram-equivalent E_q is meant the amount of substance, expressed in milligrams, complying with its equivalent mass. The milligram-equivalent E_q is determined from the ratio of the molecular mass of a substance to its valency n in a given reaction:

$$E_q = \frac{M}{n}$$ (1.4)

The equivalent of many chemical compositions is not constant since it depends on the type of reaction involved. If one considers, for instance, the reactions of neutralizing carbonic acid by caustic soda (sodium hydroxide)

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
$$NaOH + CO_2 \rightarrow NaHCO_3$$
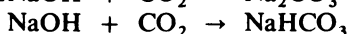
then, in the first of the reactions the equivalent of CO_2 is equal to 22, and in the second to 44. In the reaction

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2$$
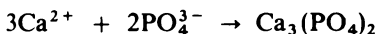
the equivalent of PO_4^{3-} is equal to 31.7, and in another similar reaction

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow 3Ca_3(PO_4)_2 \cdot Ca(OH)_2$$
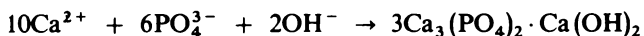
it will amount to 28.5. However, for many substances dealt with in water-treatment practice, the equivalent is constant and its value can be calculated by formula (1.4).

In this way, to express the concentration of a solution in milligram-equivalents, C_e, it is sufficient to find the concentration of the dissolved substance expressed in milligrams per litre and divide

it by the equivalent mass

$$C_e = \frac{C_{vc}}{E_q} \tag{1.5}$$

In addition to gram-equivalents, a 1000 times smaller unit is used in water-treatment chemistry, referred to as the microgram-equivalent (μg-equiv/l).

In view of the fact that in the International System of Units (SI) the fundamental unit of mass is the kilogram and the concentration of substances in steam is referred only to this unit, we shall speak below of the concentrations of substances in aqueous (water) solutions that are mainly referred to the kilogram, excepting concentrated solutions and other substances in which for a greater certainty the concentrations must be related to the litre. For dilute solutions — and the natural (raw) waters of most water-supply sources of electric power stations are precisely the solutions of this kind — no essential calculation errors are introduced when the concentration is related to the kilogram or litre. In exact calculations, however, adopted in chemical laboratories of boiler houses, concentration should be related to the litre, or density must be introduced into calculations.

1.2. Solubility of Solids in Water

A *solution* is a system in which one substance is distributed uniformly in another substance. *Saturated, unsaturated* and *supersaturated solutions* are distinguished. By a saturated solution is meant the solution in which a given substance ceases to dissolve.

The mass of a substance that must be dissolved at a certain temperature to produce a saturated solution is referred to as the solubility of the given substance.

The solubility of solids in water depends on its density ρ, dielectric constant ε that characterizes the polarity of the solvent's molecules, and on temperature. In the steam-condensate circuit of modern power stations fitted with boiler-turbine units, the temperature, density and dielectric constant of water vary within wide limits, thereby causing variations in the solubility of solids.

The solubility of some substances (NaCl and others, Fig. 1.1) increases with temperature, and that of others ($CaSO_4$, Fig. 1.2) diminishes. The solubility of some compounds (Na_2CO_3, Na_2SO_4 and others) depends on temperature in an intricate way as
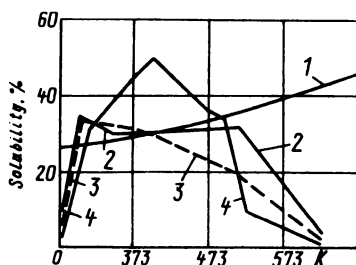
Fig. 1.1. Solubility of some sodium salts

1 - NaCl; *2* - Na$_2$SO$_4$; *3* - Na$_2$CO$_3$; *4* - Na$_3$PO$_4$
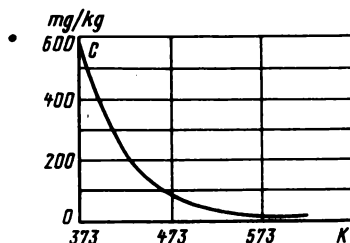
Fig. 1.2. Solubility of CaSO$_4$ · · H$_2$O
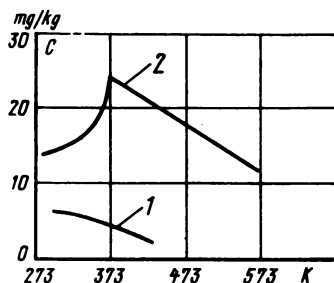
Fig. 1.3. Solubility of

Mg(OH)$_2$ (*1*) and CaCO$_3$ (*2*)
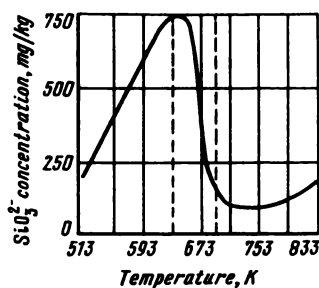
Fig. 1.4. Solubility of silicic acid in water vapour at 30 MPa

illustrated in Figs 1.1 and 1.3. The solubility of silicic acid drops sharply in the range of maximum heat capacity of the solvent at 633 to 693 K (Fig. 1.4).

The solubility of various substances varies within wide limits. Readily soluble and difficultly soluble substances are distinguished. Examples of difficultly soluble substances are calcium carbonate, CaCO$_3$, calcium sulphate, CaSO$_4$, calcium silicate, CaSiO$_3$, calcium phosphate, Ca$_3$(PO$_4$)$_2$, magnesium hydroxide, Mg(OH)$_2$, and others.

1.3. Solubility of Gases in Water

The solubility of a given gas in water, G (mg/l), can be determined by the formula

$$G = \alpha \rho \frac{p_i}{760} = K p_i' \qquad (1.6)$$

where α = absorption coefficient referred to standard conditions, cm^3/l

ρ = gas density at standard conditions, mg/cm^3

p_i, p_i' = partial pressure of gas at standard conditions, respectively mm Hg and fractions

$K = \alpha \rho$ = absorption coefficient, mg/l

The value of α is given in Fig. 1.5.
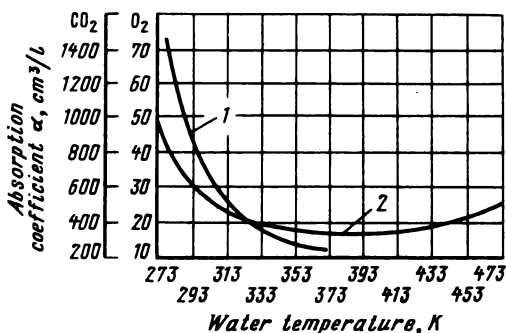
Fig. 1.5. Absorption coefficient for O_2 (*1*) and CO_2 (*2*) as function of temperature

If the total pressure, gas pressure, and the pressure of water vapour are denoted by p_t, p_g, p_{wv} respectively, then

$$p_g = p_t - p_{wv} \qquad (1.7)$$

It follows from formula (1.7) that

$$G = \alpha \rho \frac{(p_t - p_{wv}) \, \varphi}{760} \qquad (1.8)$$

where $\varphi = n_i/n$; n_i is equal to the number of moles of a given gas in a mixture of gases, and n is the total number of moles.

If water is heated, p_{wv} will grow until the equality $p_t = p_{wv}$, characterizing the state of water boiling, sets in. It is clear from formula (1.8) that the solubility of gases will then be equal to zero. This is an important conclusion and finds wide application in practice when it becomes necessary to remove dissolved gases from water by boiling.

1.4. The pH Value

Molecules of water, like those of many other substances, dissociate or split into ions:

$$H_2O \leftrightarrows H^+ + OH^-$$
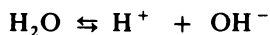
At a given temperature the product of the concentrations of these ions, g-ion/l,

$$K_w = C_{OH^-} \cdot C_{H^+} \tag{1.9}$$

is constant; this quantity is referred to as the *ion product* of water. For instance, at 298 K, $K_w = 10^{-14}$. The reaction of a medium is assumed to be neutral if $C_{H^+} = C_{OH^-}$, g-ion/l. For this case we can write

$$C_{H^+} = C_{OH^-} = \sqrt{K_w} = 10^{-7}$$

It is clear that in an acid medium C_{H^+} must be greater than 10^{-7}, and in an alkali medium $C_{H^+} < 10^{-7}$; for ions, OH^-, on the contrary, C_{OH^-} is greater than 10^{-7} in an alkali medium and smaller than 10^{-7} in an acid medium. It is inconvenient to deal the contrary, C_{OH^-} is greater than 10^{-7} in an alkali medium and using ion concentrations, H^+ and OH^-, the logarithms of the reciprocals of the hydrogen-ion concentrations are used, expressed in gram-ions per litre. The logarithm of the reciprocal of hydrogen-ion concentration is called the hydrogen value and denoted by pH, i.e.,

$$\log_{10} \frac{1}{C_{H^+}} = pH$$

The expression $pOH = \log_{10} 1/(C_{OH^-})$ will be referred to as the hydroxyl value. It follows that after the logarithm is found, equality (1.9) can be reduced to the form

$$pK_w = pOH + pH = 14 \, (t = 298 \text{ K})$$
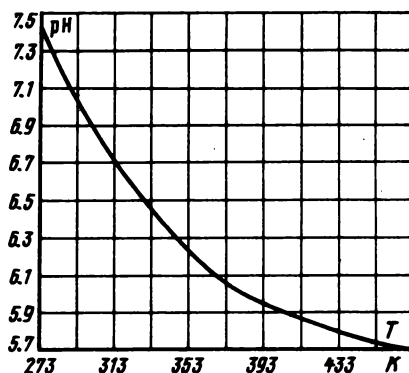
Fig. 1.6.   pH of pure water versus temperature

The neutrality requirement for an aqueous solution or water shall therefore be determined by pH = 7; an acid medium is characterized by pH < 7 and pOH > 7, and an alkali medium by pH > 7 and pOH < 7.

In Fig. 1.6, the pH value of pure water is plotted as a function of temperature. As will be shown elsewhere in the book, this dependence is of great importance for understanding the actual reaction of a medium in the condensate-vapour cycle of steam-power plants.

Review Questions

1. Name substances that are difficultly soluble in water.
2. What substances show decreased solubility with increasing temperature of the solution?
3. Name the main requirement to be observed in removing oxygen from water by boiling.
4. Give definitions of saturated, supersaturated, and unsaturated solutions. What is the state in which natural waters occur?
5. Give the definition of the equivalent.

Chapter 2

Quality of Natural Waters

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2.1. Substances
Contaminating Natural Waters

The substances contained in natural, or raw, waters can be divided into the following three groups: coarsely dispersed (suspended) substances, colloids, and molecular- and ion-dispersed substances.

Suspended substances are particles of sand and clay of different size, remnants of plants and other substances entrained from the surface by rain water or thawed snow and carried into open basins — rivers, lakes, ponds. The greatest concentration of these substances in surface waters is usually observed during floods. In analyzing raw waters, one usually determines the quantity of impurities contained in a unit volume of water (mg/l), without indicating their chemical composition.

Substances of both organic and mineral origin are present in water in colloidal state. The first include humic substances found in great amounts in swamp waters, which impart them a yellow or brown tinge. Contamination of raw water by organic substances results from the dying-off and decaying organisms dwelling in water, and also due to unpurified waste waters discharged by industrial enterprises into water reservoirs. Not all organic substances present in water remain in colloidal state; some of them are kept in a true solution.

Of the inorganic substances present in water, iron-, silicon-, and aluminium compounds are often contained in colloidal state. Colloidal impurities hamper proper performance of boiler units as they increase the tendency of boiler water to foaming: they also disturb the performance of anion exchangers that are irreversibly sorbing the anions of organic substances. That is why care is taken to remove as fully as possible organic substances from water in the course of pretreatment.

The group of molecular-dispersed substances includes salts and

gases that are dissolved in water. Since salts are dissociated to a considerable extent in an aqueous solution, the following ions are usually encountered in natural waters: cations, Na^+, Ca^{2+}, Mg^{2+}; anions, Cl^-, SO_4^{2-}, HCO_3. Thus, it may be assumed that natural waters generally contain the following compounds: $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, Na_2SO_4, $NaCl$.

The six ions enumerated are most widespread, but other ions are also encountered in natural waters. Tests often reveal that natural waters contain the following ions usually in small quantities: nitrite acid ions, NO_2^- (nitrites), nitrous acid ions, NO_3^- (nitrates), and ammonium cations, NH_4^+. The presence of these nitrogen compounds in water is indicative of the contamination of the water basin by industrial waste waters or by decomposition products of organic substances.

Ferrous compounds are also encountered in natural waters. An increased content of these impurities is characteristic of many underground (artesian) waters.

In underground waters, iron usually occurs in the form of ferrous bicarbonate, $Fe(HCO_3)_2$, which is stable only in the presence of large quantities of CO_2, whose removal from water results in decomposition of $Fe(HCO_3)_2$ followed by the formation of ferrous hydroxide, $Fe(OH)_2$. This reaction is used in the deferrization of ground waters: the water containing iron is sprayed (aerated) or air is blown through it to remove carbon dioxide. The compound $Fe(OH)_2$ being formed is oxydized by air oxygen into $Fe(OH)_3$, which is then removed from the water after its precipitation. Ferrous compounds form a precipitate capable of scaling on boiler heating surfaces.

All natural waters also contain gases, of which oxygen and carbon dioxide should be especially pointed out as they cause corrosion of metals. That is why treatment of boiler feedwater must include degasification.

2.2. Main Quality Characteristics of Water

2.2.1. Alkalinity

By alkalinity of water is understood the total content in water of substances that cause an increased concentration of ions, OH^-, upon dissociation or as a result of hydrolysis. The alkalinity of

natural waters is usually due to the presence in them of ions, HCO_3^-, SiO_3^{2-}, $HSiO_3^-$, and sometimes of CO_3^{2-} (and also to the presence of salts of some weak organic acids, known as humates) that bind H^+ ions as a result of hydrolysis, thereby increasing the concentration of OH^- ions. In addition to the above enumerated substances, the alkalinity of boiler water is also conditioned by the presence of PO_4^{3-} and OH^- ions.

Depending on the anion that is present in water (HCO_3^-, CO_3^{2-} or OH^-), alkalinity is classified respectively as *bicarbonate* alkalinity A_b, *carbonate* alkalinity A_c or *hydrate* alkalinity A_h.

The total alkalinity A_t of water is determined by the amount of acid spent together with a methyl orange indicator for water titration, and consequently it is due to the presence of not only ions, HCO_3^-, CO_3^{2-}, and OH^-, but also to other ions that react with acid, including humates.

2.2.2. Hardness

The total hardness in water, H_t, is defined as the summary concentration of calcium and magnesium cations, expressed in milligram-equivalents per kilogram (mg-equiv/kg), microgram-equivalents per kilogram (µg-equiv/kg).

By hardness and alkalinity, natural waters can be subdivided into two groups, *nonalkaline* and *alkaline*. Waters of the first group are characterized by the inequality $H_t > A_t$, and those of the second group by $H_t < A_t$. The waters of the first group, which are more frequently encountered in nature, are characterized by the following kinds of hardness: total (H_t), carbonate (H_c), noncarbonate (H_{nc}), calcium (H_{Ca}) and magnesium hardness H_{Mg}, which are related as follows:

$$H_t = H_c + H_{nc} = H_{Ca} + H_{Mg} \tag{2.1}$$

Water hardness is said to be carbonate if the water contains calcium and magnesium bicarbonates; noncarbonate hardness is due to the presence of chlorides and sulphates of calcium and magnesium; calcium hardness results from calcium compounds, and magnesium hardness from magnesium compounds.

For waters of the second group, the concepts of carbonate and noncarbonate hardnesses are meaningless because $C_{HCO_3^-} > H_t$.

These waters are characterized by a total hardness, calcium hardness, magnesium hardness, and also by alkalinity. When calcula-

ting the processes of raw water softening and internal boiler water treatment by means of precipitating agents, and also other water-treatment processes to be applied to alkaline waters, it is conditionally assumed that $H_c = H_t$ and $H_{nc} = 0$, taking into account excessive concentration of HCO_3^- ions. Soft waters (chemically treated water, feedwater, condensate, etc.) feature only a total or residual hardness H_t. It should be noted that the presence of sodium compounds in water does not contribute to its hardness.

2.2.3. Total Solids

By the *total solids content* is meant the summary amount of nonvolatile substances present in water in a colloidal and a molecular-dispersed state, expressed in milligrams per kilogram (mg/kg).

The content of total solids is determined by evaporating a preliminarily filtered sample of water, then drying the remaining solids at 383 to 393 K. The amount of these substances related to 1 kg of water gives the total solids. It follows that the concept of total solids does not embrace the gases that are dissolved in water, and also the volatiles (NH_3, for instance) and the suspended solids.

In determining the content of total solids in natural waters, calcium and magnesium bicarbonates turn into carbonates, $CaCO_3$ and $MgCO_3$. In addition to the total solids, *fixed residue, mineral* and *sulphate solids* are distinguished. If the total solids are calcined for several minutes at 1073 K, their mass will diminish, yielding the fixed residue solids. The mass of the total solids diminishes due to the removal (combustion) of organic substances, evaporation of remaining moisture, decomposition of carbonates, etc. The mass can, however, increase at the expense of metal oxidation.

The quantity obtained by adding up all cations and anions detected in water under test, including CO_3^{2-}, and also Al_2O_3, Fe_2O_3, SiO_2, is called the mineral residue. If the total solids are treated with sulphuric acid, all the cations turn into sulphuric acid compounds (sulphates), the total mass of which constitutes the sulphate residue.

2.2.4. Oxidability

Oxidability characterizes to some extent the contamination of water by organic substances. It is usually expressed in milligrams of oxygen required to oxidize in given conditions the organic

substances contained in 1 kilogram of water, and is denoted mg/kg O_2. Oxidability is not identical *with the content of organic substances in water, since under the conditions in which oxidability is determined no complete destruction (oxidization) of all organic substances takes place. Oxidability can also be expressed by the amount of $KMnO_4$, mg/kg, spent to oxidize the organic substances.

2.2.5. Transparency

Transparency is determined by the height (cm) of a column of water in a glass tube, through which it is still possible to discern printing (the type method) or to see two crossed black lines 1 mm thick on a white paper placed on the bottom of the glass tube (the cross method). Transparency characterizes but approximately the concentration of suspended solids, which must be determined by the weight method when accurate water tests are made.

2.2.6. Silica Content

By *silica content* is meant the concentration of silicic acid, H_2SiO_3 (expressed as silica, SiO_2), contained in initial water. The presence of SiO_2 in feedwater of boiler units, especially the ones rated at 4.0 MPa and above, causes a number of difficulties in operating power-generation equipment because of the formation of silicate scales of low thermal conductivity and similar heavy deposits on the blades and nozzles of turbines. That is why the water-treatment technology often includes a process ensuring partial or complete desilication of raw water. In modern practice silica is removed from raw water by using ionite exchangers (see Chapter 12).

The concentration of SiO_2 in natural waters varies over wide limits (from 5-10 to 90 mg/l). It diminishes with increasing salt content (mineralization) of water. The low-mineralized waters occurring in the northern regions of the USSR have as a rule high concentrations of silicic acid.

Raw natural waters contain silicic acid both in an ionic ($HSiO_3^-$) and in a colloidal state. This complicates desilication and chemical control of feed-water for boiler units, since only ion-dispersed silicic acid reacts in ion-exchange processes.

2.3. Characteristics of Natural Waters

The waters of surface sources such as rivers, lakes, artificial basins (water reservoirs), and seas are of the greatest practical importance to industry. The quality of river water depends on the feeding sources of a river, which may include surface runoff, snowmelt and waters of glaciers, swamps, rain and snow feedings, underground water, treated sewage waters of industrial enterprises and populated areas. In most rivers the chemical composition of water depends to a great extent on hydrometeorological conditions and the season, since the surface runoff caused by precipitation is the main water source during some of the seasons.

The soil cover which comes in close contact with the precipitated water plays a great part in the formation of the composition of natural waters. When water is filtered through peaty or boggy soil poor in salts, it becomes more contaminated with organic substances than with mineral substances. On the contrary, black earth and chestnut (brown) soils, especially alkaline soils, contaminate water mainly with mineral substances. The base rocks of soil have a still greater effect on the resultant composition of water that comes into contact with the base rocks as it seeps through the soil. They contaminate water with mineral substances, including scale-forming ones.

The composition of natural water is also greatly influenced by the climate. Heavy atmospheric precipitation humidifies the soil and is responsible for greater runoffs which reduce the mineralization of natural waters. On the contrary, small amounts of precipitation (rainfall, snowfall) result in a greater mineral residue of water. In the north, for instance, soils are fairly washed by a large amount of precipitation, and therefore natural waters are poor in minerals. In arid areas soils are rather rich in easily soluble salts, so that water has a high total solid content. That is why the mineralization of river water increases on the greatest part of the European territory of the USSR, from the North to the South-East, and on the Asian territory, from the North to the South-West.

With respect to the mineral (fixed) residue, mg/l, river waters can be subdivided conditionally into the following groups:

<div style="margin-left:2em">

waters of low mineralization . . . . . . up to 200
waters of medium mineralization   . . . . 200 to 500
waters of increased mineralization . . . . 500 to 1000
waters of high mineralization . . . . . . over 1000

</div>

During spring thawing or rainy seasons, the surface runoff is the heaviest. The salt content of these waters is small, and therefore during the flood period the hardness, alkalinity, and the total solids of river water decrease considerably. On the contrary, suspended solids and organic impurities heavily contaminate water in this period because they are washed off by water from the top mantle of soil. In addition to spring floods, there may be autumn floods, and for rivers with snowmelt and glacial feeding, summer floods are also possible. After the floods are over, mineralization of water increases gradually and reaches a maximum in winter or in a dry season, when the fraction of the "base flow" of rivers becomes predominant. The seasonal changes in the quality of water in surface sources must be taken into account in designing water-treatment plants.

Compared with surface waters, the composition of underground, or subterranean, waters depends to a great extent on the depth of occurrence rather than on hydrometeorological conditions. Underground waters feature a higher content of minerals, the almost complete absence of suspended substances (solids), and a higher content of free carbon dioxide. The chemical composition of underground waters in deep water-bearing horizons is practically constant and independent of hydrometeorological factors.

The composition and the minerals content of water in stagnant open water bodies and lakes greatly depend on the climate (dry or humid), the inflow of river water and its quality, the outflow of water and the quantity of water evaporating from the water basin. The content of total solids in mid-ocean water reaches 35 to 37 thousand mg/kg. Some seas, however, have waters of lower mineralization because of rich inflow of river water. So, the mineralization of water in the Baltic sea reaches $8 \cdot 10^3$ mg/kg, in the Black sea $(17 \text{ to } 18) \cdot 10^3$ mg/kg, in the sea of Azov $(11 \text{ to } 12) \cdot 10^3$ mg/kg, in the Aral sea $(10 \text{ to } 12) \cdot 10^3$ mg/kg, and in the Caspian sea $(20 \text{ to } 25) \cdot 10^3$ mg/kg. The main ions in ocean water are of the sodium (30 per cent) and chlorine (55 per cent) types.

Review Questions

1. Name substances that are dissolved in natural waters.

2. What nitrogen compounds may be present in natural waters? What are the sources of these substances?

3. 1.2 mg-equiv/kg of $Ca(OH)_2$ is dissolved in distilled water. Is the solution hard or alkaline? What are the values of hardness and alkalinity?

4. What factors affect the quality of natural waters?

Formation of Depositions in Boiler Units and Heat Exchangers. Deposition Prevention Measures

3.1. Composition, Properties and Quantity of Depositions

Various physical-chemical processes develop in boiler water, which cause the destruction of some compounds and the formation of others. They result from the action of heat and reagents and also arise due to evaporation. The processes often lead to the appearance of poorly soluble substances that precipitate from supersaturated solutions and form under certain conditions scale or sludge.

Scale is the name given to sufficiently dense deposits appearing on heating or cooling surfaces and capable of disturbing normal operation of a boiler unit or heat exchanger. Friable loose deposits, resulting from the settling, accumulation and thickening of suspended substances formed in water, are referred to as *sludge* deposits or simply sludge. The suspension forming in the water and the slimy accumulations in the drums of boiler units, waterwall headers and in various tanks are also often referred to as sludge. Scale and sludge are a likewise hazard to boiler units.

Depositions can be described by their physical properties and chemical composition. Among the physical properties used for the purpose are colour, hardness, porosity, adhesive force between the deposition and metal, thickness, distribution over the surface, and location in an apparatus. The chemical composition of depositions is usually characterized by the percentage content of CaO, MgO, CuO, SO_3, SiO_2, Fe_2O_3, Fe_3O_4, Al_2O_3, P_2O_5, and also by the quantity of volatiles.

For practical purposes it is important to know the composition of depositions, since it usually enables one to reveal the factors responsible for their formation. A chemical analysis (or test) elucidates the kind and origin of oxides and their relative quantity. It

fails, however, to be indicative of the particular compounds that are present in the depositions. An answer to this question can be obtained by applying more intricate test methods, among which are the radiographic (X-raying), crystal-optics and thermographic methods of analysis.

The chemical composition of scales forming in steam boiler units greatly varies. Scales can, however, be subdivided into the following four groups.

1. Alkali-earth scales consisting basically of calcium and magnesium compounds such as $CaCO_3$, $CaSO_4$, $CaSiO_3$, $Ca_3(PO_4)_2$, MgO, $Mg(OH)_2$, $Mg(PO_4)_2$. Depending on which of these compounds prevails, carbonate scale, $CaCO_3$, sulphate scale, $CaSO_4$, phosphate scale, $Ca_3(PO_4)_2$, and others are distinguished. Composite scales are possible where many compounds are present in small quantities.

2. Iron-oxide scales consisting of ferric and ferrous compounds. Depositions of this kind may contain iron silicates, ferrous phosphates, $Fe_3(PO_4)_2$, sodium ferrophosphates, $NaFePO_4$, and iron oxides, Fe_2O_3, Fe_3O_4.

3. Copper scales containing considerable amounts of copper.

4. Silicate scales of various composition.

The most important property of scale of any kind is its low thermal conductivity that varies with the structure and porosity of depositions from 0.12 to 1.2 W/m K.

The formation of scale immediately results in increased temperature of tube walls exposed to flue gas. Wall temperature t_w is specified by the formula

$$t_w = t_m + \frac{\delta_{sc}}{\lambda_{sc}} q + \frac{q}{\alpha_2} \tag{3.1}$$

where t_m = temperature of medium (water)

δ_{sc}, λ_{sc} = thickness and thermal conductivity (W/m K) of scale, respectively

α_2 = coefficient of heat transfer from the tube wall to the medium (water)

Calculations and experience indicate that with a sufficiently high rate of heat flow $(q \geqslant 250 \cdot 10^3 \text{ W/m}^2)$ the metal of tubes is overheated dangerously even at a scale thickness of 0.1 to 0.2 mm.

The amount B, kg, of scale- and sludge-forming substances

introduced into a boiler unit can be determined by the formula

$$B = \frac{C_{fw}E_e D_{fw}t}{10^3} \qquad (3.2)$$

where C_{fw} = concentration of scale- and sludge-forming substances
        in feedwater, mg-equiv/kg
E_e = numerical value of equivalent
D_{fw} = quantity of feedwater, t/h
t = time, h

Since time t averages $(8 \text{ to } 10) \cdot 10^3$ hours and more, the value of B is large even at small values of C_{fw}, especially so in high-duty boiler units. Practical experience gained in operating boiler units shows, however, that not all substances introduced into a boiler unit with feedwater remain there as sludge or scale. A fraction of them, usually a rather considerable one, is discharged with blowdown water.

3.2. Formation of Depositions in Boiler Units

3.2.1. Formation of Alkali-Earth Depositions

Formation of alkali-earth depositions requires the presence in boiler water of a sufficiently high concentration of scale-forming substances, i.e. difficultly soluble compounds. If boiler water contains cations, Ca^{2+} and Mg^{2+}, and anions, OH^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}; then, under certain conditions, the interaction of cations and anions may result in the formation of one or several of the following difficultly soluble compounds: $CaCO_3$, $CaSO_4$, $CaSiO_3$, $Ca_3(PO_4)_2$, $Mg(OH)_2$, $Mg_3(PO_4)_2$, $3MgO \cdot 2SiO_2 \cdot H_2O$.

The precipitation of these compounds from boiler water becomes possible, however, only under certain conditions. One set of conditions, for example, presupposes that the product of concentrations of the dissolved ions of the difficultly soluble substance is constant at a given temperature, i.e.,

$$C_C C_{An} = SP \qquad (3.3)$$

where C_C, C_{An} = concentration of cations and anions of the difficultly soluble substance, respectively, g-ion/kg
SP = constant quantity, called the *solubility product*

With $C_C C_{An} > SP$, precipitation is inevitable, but if $C_C C_{An} < SP$, the solution is not saturated and no precipitate forms. It follows from formula (3.3) that for precipitation of, say, $CaCO_3$ to occur, a high concentration of Ca^{2+} in the solution (boiler water) is not obligatory at all.

Precipitation may take place also at a small value of $C_{Ca^{2+}}$ if the concentration of CO_3^{2-} anions is so high that the inequality $C_{Ca^{2+}} \cdot C_{CO_3^-} > SP_{CaCO_3}$ becomes valid. It may be assumed in calculations that within the 548 to 583 K temperature range the solubility product SP for $CaCO_3$, $CaSiO_3$, $CaSO_4$ is about equal to 10^{-8}. Then the formation of depositions from calcium compounds requires that the following inequality should be valid:

$$C_{Ca^{2+}} \cdot C_{\sum An} \geqslant 10^{-8} \qquad (3.4)$$

where $C_{\sum An} = C_{CO_3^-} + C_{SO_4^-} + C_{SiO_3^-}$

In Fig. 3.1 the maximum concentration of calcium ions is plotted as a function of $C_{\sum An}$. Region I is characterized by scale-free operation, and region II by the possible formation of depositions.
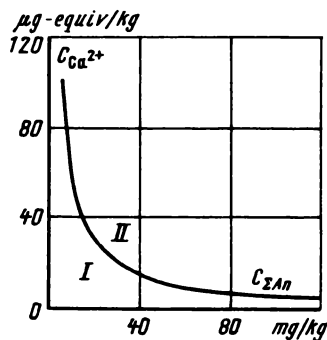
Fig. 3.1. $C_{Ca^{2+}}$ concentration versus the content of $\sum An$ in water (at $t \leqslant$ $\leqslant$ 583 K)

The rate of formation of alkali-earth depositions, A, mg/cm^2 h, depends on the concentration of scale-forming substances, C, mg/kg, and the rate of heat flow, q, W/m^2:

$$A = 1.3 \cdot 10^{-13} C q^2 \qquad (3.5)$$

Other factors are also responsible for the formation of difficultly soluble compounds, for instance, an increase in the concentration of substances in boiler water. The degree of concentration by

evaporation is specified by the expression

$$C_{ev} = \frac{C_{bw}}{C_{fw}} \tag{3.6}$$

where C_{bw}, C_{fw} denote the concentration of some compounds in boiler water and feedwater respectively.

The degree of concentration due to evaporation differs at different spots of a drum boiler unit and varies over a wide range, from 10 to 200 and above. Such spots usually originate in tubes subject to a high thermal stress (or high rate of heat flow) in the event of a sluggish or disturbed circulation, and also in the thin layer of water near the wall, where supersaturated solutions may result.

A drop in the solubility of some salts with rising temperature of the solution may also be responsible for the appearance of difficultly soluble compounds in boiler water.

Let us consider the balance of sludge- and scale-forming substances if they are present in feedwater and are introduced into a boiler unit. The amount of these substances passing into the boiler unit with feedwater per unit time is equal to

$$g_1 = D_{fw}C_{fw}$$

The amount of these substances discharged from a boiler unit with blowdown water is $g_2 = p_s D_s C_{bw}$, and with the generated steam it is $g_3 = D_s C_s$, g/h. In the foregoing, D_{fw} denotes the amount of feedwater, t/h, and, p_s identifies blowdown expressed in fractions of D_s. If $g_1 > g_2 + g_3$, the deposition in the boiler unit amounts to

$$g = g_1 - g_2 - g_3 = D_{fw}C_{fw} - p_s D_s C_{bw} - D_s C_s$$

Substituting in the above formula D_{fw} by $D_s + p_s D_s$ and cancelling D_s, we obtain the amount of the deposition, g/t (referred to 1 ton of generated steam):

$$\Delta g = C_{fw} - p_s(C_{bw} - C_{fw}) - C_s \tag{3.7}$$

When steam of normal quality is generated, it may be assumed that $C_s = 0$. Then, the condition for operating a boiler unit without scale formation is expressed by the formula

$$\frac{C_{fw}}{C_{bw}} = \frac{p_s}{p_s + 1} \tag{3.8}$$

Sulphates, SO_4^{2-}, and silicates, SiO_3^{2-}, for instance, do not precipitate in boiler units if the ratio of their concentrations in feedwater and boiler water satisfy the condition

$$\frac{C_{fw}}{C_{bw}} = \frac{C_{SO_4^{2-}fw}}{C_{SO_4^{2-}bw}} = \frac{C_{SiO_3^{2-}fw}}{C_{SiO_3^{2-}bw}} = \frac{p_s}{1 + p_s}$$

The inequality (at $C_s \approx 0$ and $C_{fw} \gg C_s$)

$$\frac{C_{fw}}{C_{bw}} > \frac{p_s}{1 + p_s} \tag{3.9}$$

indicates that the substance considered accumulates in a boiler unit in the form of a deposition or decomposes with the formation of a volatile compound, leaving the boiler unit with steam.

The solid phase may precipitate (or crystallize) from a solution and deposit directly on a heating or cooling surface. This phenomenon, usually resulting in the deposition of hard scales, is known as the primary process of scale formation. In the secondary process of scale formation, suspended particles first precipitate in the bulk of water and subsequently form secondary depositions that strongly adhere to the surface. Investigations have shown that the chemical composition of sludge does not generally differ from the composition of scale.

3.2.2. Formation of Iron Oxide Depositions

The recent advances in water-treatment practices and improvements in the operation of boiler units have lead to a practically full prevention of alkali-earth depositions at modern power stations and industrial boiler houses. However, depositions of another type, the basic components of which are iron oxides, copper and phosphates, present a serious problem. The fraction of iron oxides in depositions of this kind reaches 60 to 70 per cent and sometimes even more. The formation of iron oxide scales is most distinctly detected in the waterwall tubes of saline (secondary) sections, on the stretches of tubes exposed to high rates of heat flow (in the zone where burners are fitted, above and below the ignition belt, at the spots where the burner flame impinges onto heating surfaces, etc.). Iron oxide scales are most frequently detected in high-duty boiler units. The depositions concentrate mainly on the half of the perimeter of a tube that faces the boiler furnace.

The basic components of iron oxide depositions are iron oxides or iron phosphates, depending on scale formation conditions. The common cause responsible for the formation of the depositions considered is the introduction of iron into a boiler unit together with feedwater. The iron gets into feedwater as a result of corrosion processes taking place in the water-condensate circuit of electric power stations and industrial boiler houses. The rate of formation of iron oxide depositions, mg/cm² h, which greatly depends on the heat liberation per unit heating surface, q, can be determined by the formula

$$A_1 = 5.7 \cdot 10^{-14} C_{bw}^{Fe} q^2 \tag{3.10}$$

This should be borne in mind when fuel is changed and boiler units are to be fired with high-energy fuel (natural gas, mazute), or when overheavy firing is to be practiced.

Iron phosphate depositions originate on the water-side of thermally stressed steam-generating tubes and most commonly in the saline sections (or evaporation stages) of drum boiler units if the concentration of phosphates, PO_4^{3-}, is sufficiently high (over 80 mg/kg). For this reason in the USSR, maintenance rules for electric power stations restrict the concentration of PO_4^{3-} in the saline sections to some limiting values (see Subsec. 3.5.2). The formation of iron phosphate depositions on the water-side surfaces of boiler units is also possible when boiler water has low pH values. Such conditions may exist when acid phosphates are introduced into a boiler unit without exercising proper control. Honeycomb corrosion of the metal of tubes is then observed, which gives rise to iron oxide depositions along with iron phosphate depositions.

3.2.3. Formation of Copper Depositions

An average sample of some kinds of scale may contain 20 to 30 per cent of copper and more. Such depositions are said to be copper scales. In addition to copper, these scales also contain iron oxides and secondary impurities such as calcium and magnesium compounds. Copper scales are found to form in boiler units operated at different pressures, but always on sections subjected to a high rate of heat flow ($q \geqslant 200 \cdot 10^3$ W/m²) and mostly on the part of tube circumference facing the furnace. The main factor responsible for the formation of copper deposits is the introduction

of copper compounds into boiler units with feedwater. In depositions, copper is present in metallic state and in the form of oxides. It proves distributed nonuniformly over the deposition layer: the content of copper diminishes in the direction from the surface layer toward the tube wall (from 70-90 to 10-15 per cent).

3.3. Formation of Depositions in Once-Through Boiler Units

Once-through boiler units are known to be operated without blowdown. That is why all nonvolatile substances getting into a once-through boiler unit with feedwater may remain in the unit as depositions or be entrained by steam into the turbine. The solvent action of steam increases with pressure, and this predetermines an increase in the fraction of substances entrained by the generated steam and taken away from a boiler.

Once-through supercritical-pressure boiler units operated at a pressure of 25.5 MPa in set with turbines rated at 300, 500, 800 and 1 200 MW have found wide application in modern practice. In the USSR, modern electric stations are now fitted with boiler-turbine units of this kind. The operating process developing in these boiler units is distinguished by a considerable change in the density, temperature and enthalpy of the working fluid (water) along the steam-generating circuit, and also by a varying solubility of the substances contained in it (Fig. 3.2). In the circuit along which these changes occur there is a region where a comparatively small increase in temperature causes a considerable drop in density and growth of the enthalpy of the heat-transfer agent. A substantial reduction in the solubility of many substances (CuO, SiO_3^{2-}, $Mg(OH)_2$, $CaSO_4$ and others) is also observed in this region, referred to as the region of *maximum heat capacity* (or the region of *quasiphase transition*). That is why the depositions of scale-forming compounds (of calcium, magnesium, and iron oxides) are naturally distributed along the steam-generating circuit of a boiler unit in accordance with the change in their solubility; they form more intensively in the zone of quasiphase transition. Iron oxide deposits concentrate on the half of tube circumference facing the furnace, i.e. in the lower radiant section of the boiler unit where the rate of heat liberation per unit volume is maximum. The high thermal loads, equal to $(4 \text{ to } 5) \cdot 10^5$ W/m^2, and the presence of iron in the feedwater ($\geqslant 8$ to 10 µg/kg) intensify the rate of formation of iron
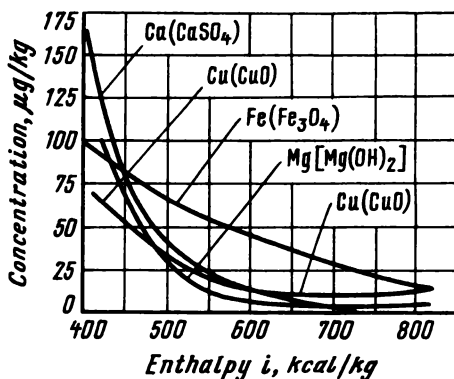
Fig. 3.2. Solubility of substances in water depending on enthalpy

oxide depositions, which causes an increase in tube wall temperature, resulting in metal overheating and possible failure of tubes.

The time, h, a boiler unit is kept in service between acid cleanings can be calculated by the formula

$$T = \frac{b_s S_a \cdot 10^3}{D_s \Delta C \cdot 1.38} \tag{3.10a}$$

where b_s = quantity of iron oxide deposits on the surface of steam-generating tubes, g/m^2

S_a = actual surface of tubes with specific contamination equal to b_s, m^2

D_s = steaming capacity of boiler unit, t/h

The rate of deposition growth, g/m^2 h, is calculated by the formula

$$w = \frac{b_s}{T} = \frac{D_s \Delta C \cdot 1.38}{S_a \cdot 10^3} \tag{3.10b}$$

where $\Delta C = C_{fw} - C_s$, and the factor $1.38 = \dfrac{Fe_3O_4}{3Fe}$

C_{fw}, C_s = concentration of Fe, $\mu g/kg$, in feedwater and main steam respectively

USSR standards restrict the value of b_s to 200 g/m². Since D_s and ΔC can always be determined in operation, and the value of S_a is taken with some approximation, the limiting values of T and w can be found. It should be emphasized that b_s and ΔC are interrelated. If their values do not agree with each other materially, the reason for it must be detected. Once-through boiler units are operated on turbine condensate with a small addition of makeup of demineralized water or distillate (1 or 2 per cent). It follows that the water-tightness of turbine condensers is the main factor determining the probability of the formation of alkali-earth deposits in once-through boiler units. As regards iron oxide depositions, their formation in small quantities is presently inevitable. There exist, however, methods that permit minimizing these deposits.

3.4. Methods of Preventing Deposition Formation in Natural-Circulation Boiler Units

3.4.1. General Aspects

The formation of depositions in drum-type boiler units is prevented by undertaking the following measures: (a) deep softening of makeup water; (b) prevention of contamination of feedwater and its components by the products resulting from the corrosion of structural materials; (c) elimination of cooling water leakage in turbine condensers; (d) internal boiler water treatment and rational chemical control of boiler water to meet prescribed standards; (e) elimination of local high rates of heat flow through steam-generating tubes.

The methods of water softening and prevention of feedwater contamination by corrosion products will be considered in other sections of the book. It should be noted here that usually it proves impossible to remove fully scale-forming agents from water in the course of its softening. The residual hardness of softened water is generally 3 to 4 µg-equiv/kg and sometimes more. The aim of boiler water treatment is to render harmless the scale formers that penetrate into the boiler unit and to eliminate their deposition on heating surfaces. For this purpose orthophosphates or salts of ethylene-diamine tetraacetic acid (EDTA) are introduced into boiler units.

3.4.2. Phosphate Treatment of Boiler Water

Cations, Ca^{2+} and Mg^{2+}, entering a boiler unit are capable of yielding difficultly soluble compounds with different anions present in the boiler water. These compounds behave differently in the boiler water. Some of them ($CaSO_4$, $CaSiO_3$) precipitate from the solution and form scale mainly on the surface of steam-generating tubes, other compounds such as $CaCO_3$, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ precipitate mainly as a suspension that turns into sludge and is removed from the boiler unit by blowdown. The object of phosphate treatment of boiler water is to create conditions under which scale formers would precipitate as loose sludge. Phosphate treatment only prevents the formation of calcium scale rather than scale in general, since triphosphate magnesium, $Mg_3(PO_4)_2$, is capable of yielding scale.

In operating natural-circulation boiler units, phosphate treatment relies on the phosphate-alkaline method and the method of purely phosphate alkalinity.

The first method secures and continuously maintains a certain concentration of PO_4^{3-} ions and free hydroxyl ions, OH^-, not bound with PO_4^{3-} in the boiler water. The second method involves the presence of only PO_4^{3-} ions in boiler water and OH^- ions bound with PO_4^{3-}. Such conditions are possible to obtain where only trisodium phosphate is present in the water. Then, the hydrolysis reaction that takes place yields PO_4^{3-} and OH^- ions in the water:

$$PO_4^{3-} + H_2O \leftrightharpoons HPO_4^{2-} + OH^-$$
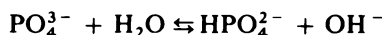
If such a solution is concentrated by evaporation, the reaction will proceed from right to left, OH^- ions will be bound by HPO_4^{2-} ions with the formation of PO_4^{3-}. Such development of the reaction makes the method of purely phosphate alkalinity highly desirable for boiler units operated at 10.0 MPa or higher and fed with condensate and demineralized makeup water, since this method prevents intergranular corrosion (see Sec. 5.4).

Phosphate-treatment is carried out using trisodium phosphate, Na_3PO_4, tripolyphosphate, $Na_5P_3O_{10}$, hexamethaphosphate, $(NaPO_3)_6$. Polyphosphates, $Na_5P_3O_{10}$ and $(NaPO_3)_6$, are potentially acid since they undergo hydrolisis in aqueous solutions with the formation of mono- and disodium phosphates (NaH_2PO_4

and Na_2HPO_4). That is why when NaH_2PO_4, Na_2HPO_4, and also polyphosphates are used, boiler water must be sufficiently alkaline to ensure their neutralization. The method of purely phosphate alkalinity commonly uses a mixture of trisodium phosphate and one of the acid phosphates, for instance $(NaPO_3)_6$. The proportion of reagents must be such that the mixture conforms to the composition Na_2HPO_4. The use of acid phosphates arises from the fact that feedwater can bring into a boiler unit HCO_3^- or CO_3^{2-} ions that yield free ions OH^-

$$CO_3^{2-} + H_2O \rightarrow CO_2\uparrow + 2OH^-$$
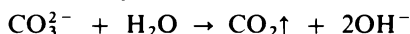
These free ions must be neutralized by HPO_4^{2-} ions:

$$HPO_4^{2-} + OH^- \rightarrow PO_4^{3-} + H_2O$$
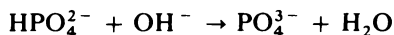
Experience indicates that practical realization of the method of purely phosphate alkalinity in supercritical-pressure boiler units (15.0 MPa), operated with demineralized feedwater, is associated with a number of difficulties. The matter is that this mode of water treatment results in an almost bufferless medium, which is practically impossible to maintain and control. This leads to the appearance in the boiler-drum primary section of various regions where pH ranges from 7 to 9.8. At some power stations, for example, prolonged water treatment of this type (with the introduction of acid phosphates) was responsible for the deposition of iron phosphates in sections of waterwall tubes exposed to high heat flow, with honeycomb corrosion detected under scale. This can be prevented by maintaining in the boiler water a ratio $A_{ph}/A_t =$ = 0.5-0.6, where A_t is the total alkalinity with a PO_4^{3-} ion concentration equal to 1 to 5 mg/kg in the primary section and not over 30 mg/kg in secondary (saline) sections.

Since hydroxylapatite contains two OH^- ions and it is exactly this compound that is desirable to obtain in phosphate treatment, care should be taken to have the medium with a sufficient concentration of these ions, i.e. the boiler water with pH in excess of 8.5. As mentioned above, nonobservance of this condition leads to the appearance of iron phosphate deposits.

Let us denote the concentration of sodium hydrate in boiler water by A_{ph} (alkaline number), mg/l, and that of PO_4^{3-} ions by Ph (phosphate number), mg/l. Then if only Na_3PO_4 is present in boiler

water, A_{ph} will be maximum:

$$A_{ph} = \frac{C_{NaOH}}{C_{PO_4^{3-}}} Ph = 0.42Ph \qquad (3.11)$$

If $A_{ph} > 0.42Ph$, purely phosphate water treatment conditions will not be ensured since free NaOH is present in water; at $A_{ph} = 0.42Ph$, boiler water control is of the purely phosphate kind, which is however very difficult to ensure in practice. The following relationship is considered optimal:

$$0.84C_{PO_4^{3-}} \geqslant 40A_t \geqslant 0.9 \cdot 0.84C_{PO_4^{3-}} \qquad (3.12)$$

When the phosphate-alkaline method of boiler water treatment is practiced, some surplus of PO_4^{3-} ions is maintained in boiler water, denoted by i_{ph}, mg/l. This value should be within 5 to 15 mg/l for boiler units operated without multistage evaporation, 2 to 6 in the primary sections, not over 30 in the saline sections of mazute-fired boiler units, and 50 in the saline sections of boiler units operated on other kinds of fuel. When the above mentioned types of phosphate treatment are used in boiler units operated without multistage evaporations, the pH value of blowdown water (at 293 K) must be not less than 9.5; in primary sections it must be not less than 9.3, and in saline sections not less than 9.5.

When a boiler unit is put into operation, a surplus amount of PO_4^{3-} must be created in the boiler water, for which purpose the following amount of phosphate is introduced into the boiler unit:

$$Ph_1 = \frac{V_b i_{ph}}{10C_{ph}} \qquad (3.13)$$

where V_b = volume of water in the boiler unit, m³
    C_{ph} = concentration of PO_4^{3-} in the commercial product introduced, %

If the boiler water already contains an initial surplus amount of PO_4^{3-}, denoted by a, mg/l, Eq. (3.13) reduces to

$$Ph' = \frac{V_b(i_{ph} - a)}{100C_{ph}}$$

During operation, phosphate is introduced continuously into the

boiler unit in the amount (g/ton steam):

$$Ph_2 = \frac{100}{C_{ph}} \left[28.5 \overset{\bullet}{H_t}(1 + P_s) + p_s i_{ph} \right] \tag{3.14}$$

where p_s = blowdown in fractions of the boiler unit steaming capacity assumed as unity

H_t = residual (total) hardness of feedwater, mg-equiv/kg

28.5 = equivalent of ion PO_4^{3-} in hydroxylapatite

The first summand determines the useful consumption of phosphate spent on binding the scale-forming substances, and the second denotes the amount of phosphate lost with blowdown water.

The water treatment ensuring purely phosphate alkalinity is applied where boiler units use turbine condensate as feedwater and distillate or demineralized water as makeup; the phosphate-alkaline treatment is applicable where chemically treated water is used as makeup. It is expedient to employ the phosphate treatment of boiler water in all drum boiler units operated at a pressure exceeding 1.6 MPa. Naturally, the best method of preventing calcium scale formation is to feed boiler units with calcium-free water. That is why concurrently with phosphate treatment, efforts should be made to reduce in every possible way the hardness of feedwater, H_{fw}. It is advisable to keep to the following minimum values of hardness:

Pressure, MPa	H_{fw}, μg-equiv/kg
1.6 = 3.9	⩽ 10
4.0 = 10.0	⩽ 5
⩾ 10.0	⩽ 3

Phosphate is introduced into boiler unit *1* as a solution of definite concentration by using either an individual or a group arrangement (Fig. 3.3). The latter is more suitable for small-capacity industrial boiler houses. A phosphate solution of 6 to 8 per cent concentration is prepared in mixing tank 6, using hot softened feedwater or condensate. When cold water is used, the solution is to be heated with steam. Pump *5* is employed to force the prepared (primary) phosphate solution through clarifying filter *4* and further into service tanks *3*, where it is diluted to the working concentration that depends on the capacity of metering pump *2* and phosphate consumption.
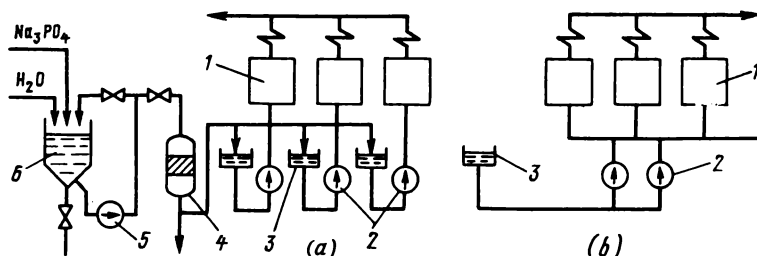
Fig. 3.3. Layout for phosphate introduction into boiler unit

3.4.3. Treatment of Boiler Water
with Complexing Agents

Phosphate treatment fails to prevent the formation of iron-oxide and cuprous depositions. This kind of treatment is associated with the formation of sludge in boiler water, and thus it can only ensure scale-free operation. It is not infrequent that phosphate chemicals themselves become a source of depositions (iron phosphates and others). In distinction to phosphate treatment, the conditioning of boiler water with complexing agents can secure scale-free and sludge-free operation of boiler units and, sometimes, also corrosion-free operation under certain conditions. These agents are referred to as complexones or complexing agents. Examples of these are the well known ethylene-diamine tetraacetic acid (EDTA), and disodium salt, known as "trylon B".

In the process of trylon treatment applied to drum-type boiler units, a 1.5 per cent or weaker solution of trylon B, alkalized preliminarily with NaOH or NH_4OH to pH = 8.5, is introduced into feedwater (at the suction of feedwater pumps). This complexing agent binds the cations of scale formers into a strong, well soluble substance of a complex structure (complexonate). The result is that sludge- and scale-forming compounds do not form in boiler units. Trylon treatment enables binding iron into a complex, reduces its carry-over with steam and thus lowers the concentration of iron in condensate. Compared with phosphate treatment, the treatment of boiler water with complexing agents reduces the carry-over of iron with steam by 50 per cent and more.

The amount of a complexing agent, g/h, spent on improving the

quality of boiler water may be calculated by the formula:
$$G = (186H_{fw} + 6.7C_{Fe} + 6C_{Cu})D_s \cdot 10^{-2} \qquad (3.15)$$

where D_s = boiler unit steaming capacity, t/h

H_{fw} = feedwater hardness, µg-equiv/kg

C_{Fe}, C_{Cu} = concentration of iron and copper in feedwater, µg/kg, respectively

The results of treatment with complexing agents depend on boiler water temperature and the quality characteristics of feedwater. The highest concentrations of calcium, magnesium and iron in feedwater are inherent in medium-pressure boiler units (4.0 MPa). In these conditions the main object of correction treatment is to prevent the formation of alkali-earth and iron-oxide depositions. The feedwater for superhigh-pressure boiler units (15.5 MPa) is usually deeply softened to have minimum hardness. Here the main object of treatment with the aid of complexing agents is to prevent the deposition of iron oxides in boiler units, reduce the carry-over of oxides with steam and protect the units against steam-water corrosion. Boiler units operated at a pressure of 10.0 MPa occupy a midposition; however, the processes developing in them in the event of treatment with complexing agents are more similar to the processes characteristic of superhigh-pressure boilers. With high-quality feedwater (with distillate or demineralized water used as makeup water), the results of treatment with complexing agents are almost the same as in boiler units operated at 15.5 MPa.

The consumption of complexing agents, calculated by formula (3.15), largely depends on feedwater hardness. That is why the use of complexing agents for correction of the water treatment process in intermediate-pressure boiler units may be justified from the economic viewpoint only under conditions at which phosphate treatment of boiler water does not prevent scale deposition on heating surfaces and fails to ensure dependable operation of metal (i.e. when heating surfaces are exposed to high rates of heat flow or liquid fuel such as mazute is fired, and in other cases). Starting at a temperature of 423 K, EDTA and complexonates (the salts of EDTA) undergo thermal decomposition, which proceeds at a high rate with growing temperature; at about 533 to 573 K the decomposition of primary complexonates terminates. The gaseous products of decomposition dissolve in turbine condensate and preserve their complexing capacity, which fact must be taken into account in practicing correction treatment of water with

complexing agents. Thus, the consumption of complexing agents, calculated by formula (3.15), can be reduced if allowance is made for the above mentioned property of decomposition products.

The layout used to prepare and meter out the EDTA solution must be made from steel, and the process of metering should be automated. When treatment with complexing agents is applied, phosphate treatment must be abandoned and amine treatment continued. It is inexpedient to create a surplus of the complexing agent in boiler water. With this kind of water treatment, the chemical control is based on the hardness of blowdown water which must be in the range between 10 and 15 µg-equiv/kg. When the pH value of boiler water exceeds 11, trylon treatment is inadmissible.

3.4.4. Alkaline Treatment of Boiler Water

When alkaline treatment is applied, the scale-forming substances penetrating into a boiler unit precipitate as $CaCO_3$ and $Mg(OH)_2$. In a nonalkaline medium (for instance, in turbine condensers), calcium carbonate falls out on heating or cooling surfaces and forms dense scale. With alkaline boiler water, calcium carbonate precipitates as a loose sludge not adhering to surfaces.

To obtain adequate results in practicing this method of water control, a certain alkalinity A_{bw} of boiler water must be maintained. For this purpose alkaline reagents are introduced into a boiler unit in a quantity (kg/h) determined by the formula (taken as a 100 per cent pure chemical product)

$$A = [H_{nc}(1 + p_s) + p_s A_{bw}]D_s E_e \cdot 10^{-3} \tag{3.16}$$

If the calcium hardness and magnesium hardness of boiler feed-water are respectively H_{Ca} and H_{Mg}, mg-equiv/kg, the amount of scale-forming substances, kg/h, penetrating into the boiler is expressed by

$$S_{sl}^{fw} = D_s(1 + p_s)(50H_{Ca} + 29H_{Mg})10^{-3} \tag{3.17}$$

and the concentration of sludge in boiler water, mg/l, is

$$S_{sl}^{bw} = \frac{1 + p_s}{p_s}(50H_{Ca} + 29H_{Mg}) \tag{3.18}$$

It is efficient to practice the alkaline treatment of boiler water

only in boiler units operated at a pressure up to 1.6 MPa, which is due to the fact that the stability of•the carbonate ion, CO_3^{2-}, depends on temperature, whose increase is followed by decomposition of soda. As a result, the effectiveness of alkaline treatment decreases and the generated steam is contaminated with carbon dioxide. If the alkalinity of feedwater is specified by the equality $A_t = A_c + A_b$ (see Sec. 2.2), then the quantity of carbon dioxide, CO_2, mg/kg, passing into the generated steam is found from the equation

$$C_{CO_2} = (1 + p_s)(A_b + aA_t)22 \tag{3.19}$$

where a is the degree of soda decomposition (in fractions).

The contamination of steam with carbon dioxide is extremely undesirable, since it induces corrosion of metal in the condensate circuit. Alkaline treatment of boiler water can be used in low-capacity boiler units operated with a rate of heat flow not exceeding 10^5 W/m^2.

It should be noted, however, that alkaline treatment is only useful where other methods of preventing scale formation prove impracticable.

3.5. Preventing Deposition Formation in Once-Through Boiler Units

The deposition of scale on the water-side heating surfaces of once-through boiler units can be prevented by eliminating the sources of feedwater contamination, of which the main are the corrosion processes proceeding in the condensate-vapour circuit (see Sec. 5.3) and leakage of cooling water in turbine condensers. Control of these contamination sources is one of the main objectives of the maintenance personnel of an electric power station.

The penetration of cooling water into the intertubular space of steam-turbine condensers is called *leakage*, ω, the value of which is determined in per cent by the formula

$$\omega = \frac{C_c - C_s}{C_{cw} - C_s} 100 \tag{3.20}$$

where C_c, C_s, C_{cw} are the concentrations of any of the compounds in condensate, steam and cooling water, respectively. The quantity

ω is often controlled through the hardness or electric conductivity of the indicated components.

To make turbine condensers sufficiently watertight, the expansion joints between condenser tubes and the tube plate are sealed by special putties which should have good adhesion to metal, be elastic and durable. Practical experience shows that it is almost impossible to eliminate fully the leakage of cooling water in condensers, since the presence of slight leakiness in the enormous number of these joints or cracks in the walls of tubes is sufficient for the concentration of impurities in condensate to exceed specified limits. It is for this reason that modern high-power supercritical-pressure boiler-turbine units operated at a pressure of 25.5 MPa are fitted with demineralizing plants (see Sec. 12.4) to remove from turbine condensate the ionic and dispersed impurities. Proper cleaning of the entire turbine condensate in the demineralizing plant is a requisite condition to be observed in organizing water control for supercritical-pressure boiler units.

Of no lesser importance is the elimination or reduction of corrosion along the condensate-water circuit of a boiler-turbine unit (see Sec. 5.3). Corrosion causes feedwater contamination with iron and copper oxides, which form depositions in the boiler unit and turbine.

It is known from experience that in boiler units iron oxide deposits form primarily in the bottom radiant heat-absorbing part exposed to high heat flows. Iron oxides usually fall out on the half circumference of tubes facing the furnace. The operating conditions of these tubes would be greatly improved if these deposits were distributed over other heating surfaces, and the boiler unit could be kept in service for a longer time before laying it off for scheduled washing.

Treatment of feedwater with the EDTA complexing agent eliminates the accumulation of iron oxides in the bottom radiant heat-absorbing surfaces. This effect of the EDTA is based on the regularities governing thermal decomposition (thermolysis) of iron complexonates that proceeds with precipitation of magnetite on tube walls. The process of thermolysis is extended along the boiler unit circuit so that most of the magnetite precipitates before the working fluid reaches the bottom radiant heat-absorbing surfaces. In operation, 70 to 80 per cent of iron oxides fall out in the water economizer of a boiler unit. The magnetite deposited on the bottom radiant heat-absorbing surfaces is compact, adheres strongly to the

metal, and its thermal conductivity is 3 to 4 times greater than that of depositions which form under .conventional conditions. The decrease in the rate of formation of iron oxide deposits on the bottom radiant heat-absorbing surfaces is due to the fact that when trylon treatment is used the rate of increase in tube wall temperature becomes 2.5-3 times smaller than when traditional methods of water control are used. A 33 to 50 per cent decrease in the amount of deposits in turbines is also recorded. Feedwater treatment with the trylon reagent is not the only means of reducing or preventing the formation of iron oxides on radiant heat-absorbing surfaces. Similar results may be ensured by applying other methods of water control (see Sec. 5.5).

3.6. Preventing Deposition Formation in Turbine Condensers

At electric power stations and various industrial enterprises much water is used as a cooling agent. Because of the limited capacities of available water-supply sources and also for the purpose of water economy, it is usual to employ closed-circuit type cooling-water systems, in which cooling water circulates in a closed cycle, i.e. it heats up in the apparatus to be cooled and cools in a spray cooling pond (or cooling tower). In water-supply systems of this kind various processes occur in the circulating water. When water is sprayed in a pond or tower, dissolved carbon dioxide, CO_2, is removed from it, resulting in a decomposition of calcium carbonate by the reaction

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

It is precisely this process that causes the formation of solid carbonate deposits in the tubes of turbine condensers. Concurrent with this process, water evaporates partly and the concentration of substances dissolved in it increases. Here concentration by evaporation takes place, the extent of which is characterized by the concentration coefficient

$$k_c = \frac{C_c}{C_m} \tag{3.21}$$

where C_c and C_m denote the concentration of nonprecipitating,

nonvolatile substances in the circulating (return) and in the makeup water, respectively.

The condition for scale-free operation of a closed-circuit cooling-water system is specified by the equality

$$H_{cc} = k_c H_{cm} \qquad (3.22)$$

where H_{cc} and H_{cm} denote the carbonate hardness in the circulating and the makeup water respectively.

If the actual carbonate hardness in circulating water, H_{cc}^a, proves lower than the calculated hardness H_{cc}, then this means that $CaCO_3$ precipitates in the closed-circuit cooling-water system in the quantity

$$\Delta H = H_{cm} k_c - H_{cc}^a \qquad (3.23)$$

In practice, care is taken to operate boiler units with a small concentration coefficient as this reduces appreciably the intensity of scale formation. This can be attained by blowing down the system. The amount of blowdown, in per cent of the total quantity of water circulating in the system, Q_c, can be calculated by the formula

$$p_{bd} = p_1 \frac{C_m}{C_c - C_m} 100 = p_1 \frac{1}{k_c - 1} 100 \qquad (3.24)$$

where p_1 is the amount of water lost by evaporation in fractions of the total amount of circulating water.

The water discharged from the system by blowdown is replaced by makeup water, added in the same amount. The amount of makeup in per cent of Q_c is determined by the formula

$$p_m = p_1 \frac{C_c}{C_c - C_m} 100 = p_1 \frac{k_c}{k_c - 1} 100 \qquad (3.25)$$

The closed-circuit cooling-water system is blown down in two ways: a fraction of water is carried over by air in droplets, p_2, the other, p_3, is discharged from the system in conventional manner and is referred to as blowdown proper, i. e. $p_{bd} = p_2 + p_3$.

The formation of carbonate deposits in turbine condensers is prevented by treating makeup water in one of the following ways: acidification, lime treatment, phosphate treatment, recarbonization.

For acidification, sulphuric acid is usually introduced into

makeup water, which results in the destruction of HCO_3^- ions and formation of carbon dioxide, CO_2:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$
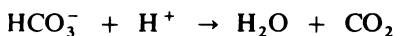
In consequence, the carbonate hardness in water diminishes and the concentration of free carbon dioxide increases. All this terminates decomposition of calcium bicarbonate. In the course of acidification, it is rather important to meter out correctly the amount of acid introduced into water. An increased dose of acid raises the corrosive ability of water, and a small dose fails to ensure scale-free operation.
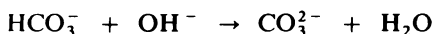
The treatment of water with lime, $Ca(OH)_2$, also causes the destruction of HCO_3^- ions, though without formation of CO_2:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

In distinction to acidification where only a small fraction of HCO_3^- ions are destroyed, lime treatment removes all bicarbonate ions from the water. Lime treatment, to be considered in detail in Chapter 9, is rather seldom applied to return water circuits, since this involves the construction of an expensive plant.

The essence of phosphate treatment consists in that phosphates introduced into water deprive calcium carbonate of its scale forming properties. Up to the present the processes associated with this method of water treatment have not been sufficiently studied. It must be emphasized that phosphates are capable of preventing carbonate deposition only at rather small concentrations, about 3 to 4 mg/l PO_4^{3-}. Large concentrations cause the opposite effect, namely, water softening and precipitation of sludge. Used as reagents are superphosphate, trisodium phosphate and hexametaphosphate. The latter chemical proves more effective than the first two, but orthophosphates are more available and cheaper. Water treatment with orthophosphates and acid is often applied when the carbonate hardness of makeup water is high.

Treating water with gases containing CO_2, in particular with the furnace gas from boiler units, is aimed to increase the concentration of free carbon dioxide in the water. For this purpose the gas is blown through the layer of water, or mixed with the water by means of a water-operated ejector, with the result that CO_2 contained in the gas dissolves in the water. Just as in the case of acidification, the saturation of water with carbon dioxide terminates

the decomposition of bicarbonate ions. When water is treated with the furnace gas, the SO_2 component of the gas plays an important part.

In addition to mineral (carbonate) depositions, condenser tubes often become overgrown with organic substances due to a variety of microorganisms that settle on the water side of tubes. They form a slimy or gelatin-like film with grey-green or brown tinges, which affects the vacuum in tubes. The overgrowing of tubes with microorganisms is controlled by treating cooling (circulating) water with •chlorine or chlorinated lime that destroys (acidifies) the microorganisms.

3.7. Preventing Deposition Formation in Heat-Distribution Systems

Heat and electric power stations supply steam and hot water to consumers. Hot water is heated in heaters (boilers) and delivered to heat-distribution systems that supply the hot water to individual consumers. The amount of water supplied to a heat-distribution system, called the makeup, is equal to the loss of water due to leakage in the system. According to the adopted regulations, the average annual leakage should not exceed 0.25 per cent of the total volume of water filling the heat-distribution system and the pipelines of associated consumers.

In up-to-date heat-distribution systems, the loss of water due to leakage is compensated for by adding chemically treated (i. e. sufficiently softened) makeup water. That is why the problems associated with alkali-earth depositions in pipelines and on heating surfaces of such systems do not occur at all. However, heat-distribution systems are often contaminated with iron oxides, whose elimination presents sometimes much difficulty.

The main sources responsible for the appearance of iron oxides in the water of heat-distribution systems are the processes of corrosion taking place within the water-heating boiler house (in the circuit upstream and downstream from the deaerator and in storage tanks) and in the hot-water supply mains. Corrosion is caused by the oxygen penetrating periodically or continuously into the heat-distribution system due to the fact that makeup water is not deaerated sufficiently. During the period of peak loads, in open systems insufficiently deaerated water is sometimes used as makeup. All this contributes to the accumulation of iron oxides in the

system. Experience shows that all the oxygen penetrating into a system causes corrosion within a radius of about 1.5 to 2.0 km.

The measures taken to prevent the deposition of iron oxides can be divided into two groups. The first group includes measures taken to reduce or eliminate completely the penetration of oxygen or carbon dioxide into the heat-distribution system by improving the performance of vacuum deaerators that handle makeup water, alkalizing water in the system, rationally delivering water to storage tanks, preventing contact between the water surface in tanks and the steam-air mixture. Corrosion is controlled successively by the use of dissolved sodium silicate (water soluble glass), whose concentration in hot-water supply and district-heating lines is maintained within 12-16 mg/kg SiO_2 at pH = 7.2-6.5.

The second group relates to the removal of accumulated iron oxides from the equipment and pipelines; it includes such measures as acid cleaning of boilers and heat-distribution systems, water-air washing of heaters and local heating systems, filling of laid-off heaters and local heating systems with sodium silicate solutions.

3.8. Removal of Deposits

The deposits formed in a boiler unit or in a heat-exchange apparatus are removed mechanically or chemically, depending on local conditions. The mechanical method involves the use of various scraper-type and cutting tools (wire brushes, for example). This method is suitable for small boiler units and simple heat exchangers. The chemical method provides for cleaning of heating surfaces with solutions of chemical reagents — alkalis, acids and complexing agents. Two kinds of chemical cleaning are distinguished: cleaning of newly installed boilers before putting them into operation (prestarting cleaning) and planned cleaning of boilers while in service. The aim of prestarting cleaning is to remove rust, welding rag, burrs, iron scale and other impurities. Planned or s heduled cleanings in the course of service permit the removal of all kinds of deposits formed in operation.

Modern newly installed high-capacity boiler units of electric power stations must undergo chemical cleaning before being put into operation. Cleaning is initiated by intensive water washing at a rate of 1.0-1.5 m/s for drainable and 2.0-2.5 m/s for nondrainable surfaces, first with cold water, discharged into sewerage, then with circulating hot water (up to 373 K). The next operation is boiling-

out (to remove silicates, oils, etc.) with a 0.5-1.0 per cent solution of NaOH for drum-type boiler units and with a solution of NH_4OH when dealing with once-through boilers. Other reagents can also be used (detergents, for instance). Boiling-out is followed by the treatment with the aid of reagents that remove iron oxides (rust, iron scale). When a boiler unit undergoes a scheduled cleaning, the first two operations are omitted.

The reagents used for the purpose include hydrochloric acid and a number of organic acids such as citric acid, maleic acid, and also the EDTA complexing agent. The most available and cheapest of the cleaning chemicals is hydrochloric acid, usually used for cleaning small-capacity boiler units of industrial boiler houses and heat exchangers, including turbine condensers. This chemical is, however, of limited usefulness for high-capacity units, especially supercritical-pressure boiler units, due to the metal-attacking properties of this acid and the intricate layout of cleaning. Organic acids are less aggressive and possess other advantages over HCl. However, they are consumed in large quantities, which increases cleaning expenditures and causes difficulties involved in treatment of the waste water. The most suitable reagent is found to be a mixture of the EDTA complexing agent and organic acid taken in the proportion 1 : 1, though other proportions are also admissible. Experience has shown that the mixture of EDTA with an organic acid (best of all with citric acid) has a number of advantages, and therefore it is most often used for prestarting cleaning.

For scheduled washings, reagents and mixtures are selected depending on the chemical composition of deposits, their properties and structure. Various cations are transferred into complexonates under different conditions. The optimal values of pH of a solution that are required for the formation of complexes with various cations are given in Fig. 3.4. The negative logarithms of the constant of chemical resistance, pK, for the complex being formed are plotted on the X-axis. The compositions must be as little aggressive as possible, ensure proper cleaning for a short time, and also guarantee the dissolution of all deposits and permit a comparatively simple treatment of waste water to render it harmless. Preference should also be given here to compositions containing the EDTA complexing agent and organic acid. Upon removal of the deposits the solution is displaced from the boiler unit by water, and boiler surfaces are then washed to get rid of residual impurities. The washing operation is followed by neutralization of the acid reagent

with an alkaline solution. The cleaning is terminated by passivating the metallic surfaces. The following kinds of passivation are applied to boiler-turbine units operated at supercritical pressures: nitrite-ammonium, hydrazine-ammonium and complexon passivation.
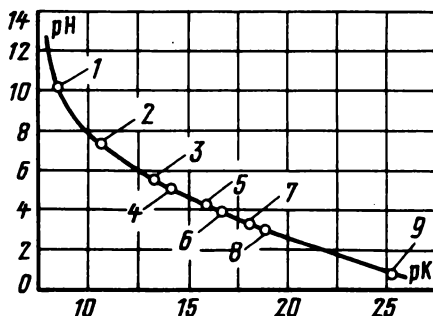

Fig. 3.4. Optimal values of pH of solution for the formation of EDTA-base complexes with various ions

1 — Mg; *2* — Ca; *3* — Mn; *4* — Fe^{2+}; *5* — Zn. Co; *6* — Cd; *7* — Cu; *8* — Ni; *9* — Fe^{3+}

Chemical washing of equipment is a very demanding operation and must be carried out by experienced personnel. The operation is preceded by the analysis of deposits, choice of reagents, working-out of the flowsheet and the washing layout, erection of equipment in compliance with the layout which can be sometimes rather complicated and cumbersome; elaboration of the layout for collection of solutions and selection of the method of their neutralization; selection of the scope and method of chemical control to be practiced. All this makes chemical washing an expensive and labour-consuming operation.

The use of complexing agents makes it possible to simplify considerably the process of cleaning and reduce the expenditures involved in scheduled cleanings. One of these methods is "cleaning while in operation", which is based on the ability of complexing agents to form well soluble complexes with all cations present in boiler water. If a complexing agent is introduced into a drum-type boiler unit in which there are contaminating deposits on the water-side surfaces, these deposits will be gradually dissolved and

removed from the boiler unit by blowdown. As already mentioned, however, the removal of large deposits in this way may prove disadvantageous due to the high cost of the complexing agent.

It may turn out to be efficient to clean small boiler units of industrial boiler houses by boiling out the alkali-earth deposits through the use of alkaline (Na_2CO_3) or phosphate (Na_3PO_4) chemicals. This treatment makes deposits softer, which facilitates their subsequent removal from boiler units by mechanical cleaning.

Review Questions

1. What substances precipitate in boiler units in the form of scale and what are their basic properties?

2. What part does the heat flow play in scale formation? What measures should be taken to prevent scale formation?

3. Describe the methods of water treatment applied to prevent the formation of scale in drum-type boiler units.

4. What are the methods of preventing scale formation in supercritical-pressure once-through boiler units?

5. Describe the methods of removing deposits.

Chapter 4

Steam Contamination and Methods of Contamination Control

4.1. Entrainment of Substances by Saturated Steam

The quality of steam generated in boiler units is determined by the quantity of various substances contained in it — nonvolatile and gaseous — regarded as impurities. It is characterized by the salt content of steam, which is the total concentration of nonvolatile substances in steam, expressed in mg/kg (or µg/kg). The quality of steam is most often described by the amount of Na, SiO_2, and CO_2 contained in the steam.

Experience indicates that the steam generated in boiler units always contains various substances that get into it from the boiler water. The phenomenon of transfer of substances present in the boiler water into the steam is called the *distribution* of substances between the liquid and the vapour (gas) phase. The ratio between the quantities of substances distributed in both phases is known as the distribution coefficient

$$K'_d = S'_s / S'_{bw} \tag{4.1}$$

where S'_s, S'_{bw} = concentration of the total quantity of any substance (or the sum of many substances), in steam and boiler water, respectively, mg/kg.

The true (K_{dt}), apparent (K_{da}) and total (K'_d) distribution coefficients are distinguished. The magnitude of K_{dt} characterizes the distribution of a given substance of certain form (molecules, for instance); the apparent distribution coefficient specifies the distribution of a given substance in all forms. The coefficient K_{dt} is determined by the equality

$$K_{dt} = \frac{S_s}{S_{bw}} \left(\frac{\rho_s}{\rho_w} \right)^n \tag{4.2}$$

where ρ_s, ρ_w = densities of steam and water respectively, kg/m^3
n = exponent (coordination number) characterizing the nature of substance

The magnitude of K_{dt} increases with pressure and temperature, most intensively for substances with a large value of n (for SiO$_2$ n is equal to 1.9; for NaCl, 1.9; MgO, 3.1; CaO, 5.5; and for NaOH, 4.1) [9]. Of these substances we must single out SiO$_2$, Fe$_3$O$_4$, and CuO that greatly impair the performance of boiler units, especially supercritical-pressure units. The solubility of these substances in steam at high pressures is considerable; their concentration in steam can only be diminished by decreasing in any possible way their concentration in feedwater.

The quantity $S'_s = K'_d S'_{bw}$, μkg/kg, may be referred to as *carry-over*. *Droplet* and *selective* kinds of carry-over are distinguished. Carry-over is said to be of the droplet kind when impurities get into the steam mostly with boiler water droplets taken away from the boiler-unit drum. With droplet carry-over, the quantity of various substances contained in steam is proportional to their concentration in the boiler water, which can be expressed by the following set of equalities:

$$K_d^t = \frac{C_{Cl^-}^s}{C_{Cl^-}^{bw}} = \frac{C_{SO_4^{2-}}^s}{C_{SO_4^{2-}}^{bw}} = \frac{C_{SiO_3^{2-}}^s}{C_{SiO_3^{2-}}^{bw}} = \frac{S'_s}{S'_{bw}} \tag{4.3}$$

where the indices s and bw indicate the concentrations of substances in steam and boiler water.

Droplets of moisture originate in the drum of a boiler unit mainly as a result of two processes: breaking of water and destruction of steam bubbles. Water usually breaks into particles as the jets of the steam-water mixture entering the steam space of the drum strike all kinds of baffles and partitions that are placed on the paths of the jets so as to quench their kinetic energy. Such impacts result in the formation of droplets of different size. The higher the velocity of a steam-water jet entering the drum, the finer the droplets that form as the jet strikes a baffle. Fine droplets are easily entrained by the steam leaving the drum. That is why in designing and constructing drum internals, water breaking processes must be minimized or precluded altogether.

The second source of the formation of droplets is the rupture of steam bubbles, which shows up materially when the steam-water mixture is introduced into the drum below the level of boiler water.

The rupture of steam bubbles is accompanied by the formation of fine droplets that are thrown into the vapour space in all directions. If the initial kinetic energy of a droplet is sufficiently large, the droplet will be thrown to a greater height. The droplet may reach the steam separating devices and be entrained by the steam flow into the steam superheater. The greater the height of the steam space in a boiler drum, the smaller the possibility of the entrainment of such droplets since they gradually lose energy and fall down.

Carry-over is said to be selective when some substance or a group of substances passes into the steam in larger quantities as
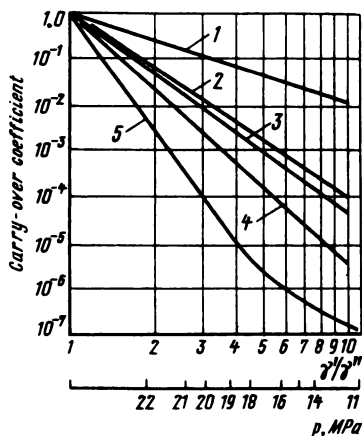

Fig. 4.1. Carry-over coefficient for various salts versus steam pressure

1 — SiO$_2$; *2* — NaOH; *3* — NaCl; *4* — CaCl$_2$; *5* — Na$_2$SO$_4$

compared to other substances. Equality (4.3) does not hold then for some substances. Selective carry-over becomes appreciable (due to the solubility of substances in steam) at a pressure of 7.0 MPa and higher. The origination of selective carry-over is traced to the fact that individual substances contained in boiler water are able to dissolve in high-pressure (and temperature) steam. A distinctive representative of such substances is silicic acid, H$_2$SiO$_3$, whose solubility in steam increases rapidly beginning with a pressure of 7.0 MPa.

In addition to silicic acid, other substances ($NaCl$, Na_2SO_4) show a tendency toward selective carry-over at high pressures. The carry-over coefficient of various salts is plotted as a function of steam pressure in Fig. 4.1. Silicic acid possesses the greatest solubility in steam, and sodium sulphate the smallest. The solubility of substances in steam increases with pressure. In supercritical-pressure boiler units, therefore, selective carry-over becomes the main source of saturated steam contamination.

4.2. Factors Affecting the Quality of Steam Generated in Natural-Circulation Boiler Units

4.2.1. Design Features of Boiler Unit

The quality of saturated steam depends on many factors, including the design features of a boiler unit: the height and volume of the steam space in the boiler drum; the way of introducing the steam-water mixture into the drum, the method of steam separation and discharge from the drum (Fig. 4.2), efficiency of drum internals and other factors.

The most important parameters predetermined by the design of a boiler unit are the rate of evaporation per unit drum steam space, R_d, and per unit evaporating surface, R_s. The average specific rate of evaporation per unit steam space, m^3/m^3 h, is determined by the formula

$$R_d = \frac{D_s v'' \cdot 10^3}{V_{ss}} \tag{4.4}$$

where v'' = specific volume of steam, m^3/kg
 V_{ss} = steam space of drum, m^3

It follows from equation (4.4) that the residence time of steam in the drum steam space is $\tau = 1/R_d$.

A decrease of τ with increasing R_d is indicative of a growing steam velocity in the steam space.

The steam space of a drum may be loaded nonuniformly. Then the rate of evaporation for individual sections of the steam space may appreciably exceed the average rate of evaporation, R_d. Such sections serve as a steam contamination source. A local high rate of
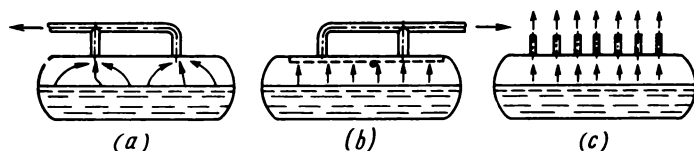
Fig. 4.2. Methods of steam extraction from boiler-unit drums
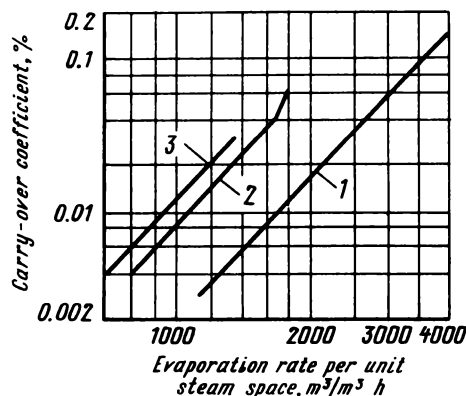
(a) concentrated; (b, c) uniform

Fig. 4.3. Steam wetness versus rate of evaporation per unit drum volume

1 — 3.6 MPa; *2* — 9.2 MPa; *3* — 11 MPa

evaporation in the steam space originates due to various reasons. It is most frequently caused by a nonuniform steam release from the drum or by concentrated introduction of the steam-water mixture into it. Improper operation of drum internals or their irrational design and layout also contribute to a local overloading of the drum space. The effect of R_d on the water content of steam is illustrated in Fig. 4.3.

When the steam-water mixture is introduced into a drum below the boiler water level, steam bubbles run through the bulk of boiler water and pass into the steam space through the evaporating surface. In this connection the rate of evaporation from the surface of

boiler water, m^3/m^2 h, is of vital importance:

$$R_s = \frac{D_s v'' \cdot 10^3}{F_s} \qquad (4.5)$$

With account taken of the units of measure, the quantity R_s may be said to characterize the linear velocity of steam flow through the evaporating surface. When the steam-water mixture is introduced below the level of boiler water, the carry-over or the amount of moisture entrained by the steam is mainly determined by the magnitude of R_s and the actual height of the steam space (with regard for swelling). Hence to reduce the water content of steam, either R_s must be decreased or h_d^{ss} increased (Fig. 4.4).
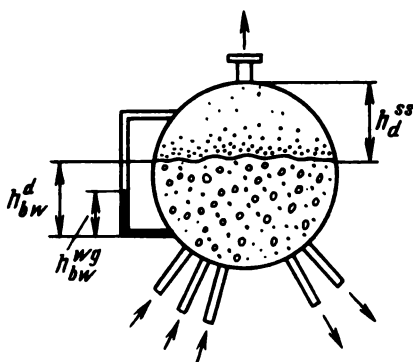

Fig. 4.4. Water swelling in drum

Steam bubbles move through the layer of boiler water, h_{bw} thick, m, with some velocity v_s, m/s. This means that the bubbles remain for some time in the water, equal to $\tau_s = b_{bw}/v_s$.

The lower the velocity, the longer the steam bubbles reside in the boiler water, so that the water becomes saturated with steam and changes to a steam-water mixture, the density of which, ρ_{mix}, is markedly smaller than that of water, ρ'. In consequence, the volume of water grows, its level in the drum rises, and thus the steam space decreases. This phenomenon is referred to as *swelling* of boiler water. Swelling results in that the level of boiler water in the drum, h_{bw}^d, becomes higher than the level h_{bw}^{wg} indicated on the water gauge

glass, as shown in Fig. 4.4:

$$h_{bw}^{d} = h_{bw}^{wg} \frac{\rho'}{\rho_{mix}} \tag{4.6}$$

As a result the height of the steam space diminishes, which materially affects the steam quality, as can be seen in Fig. 4.5. It follows that the delivery of the steam-water mixture below the evaporating surface entails water swelling in the drum. In these conditions concentrated feed of the steam-water mixture is particularly undesirable, since it creates high local rates of steam flow through the evaporating surface, resulting in an intensified increase in the content of water in steam. In practice, measures are
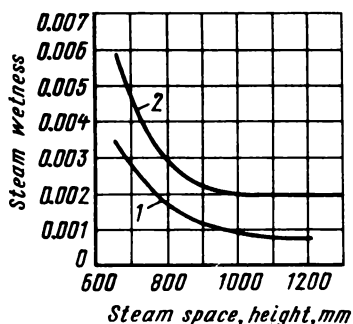

Fig. 4.5. Steam wetness as function of steam space height

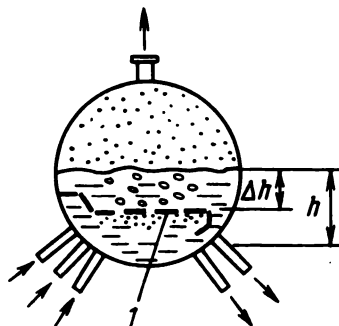*1* — 11.0 MPa, $R_s = 100$ m³/m² h; *2* — 18.5 MPa, $R_s = 50$ m³/m² h

Fig. 4.6. Water-steam separation with perforated plate placed in water

always taken to have the evaporating surface loaded uniformly. One of the most widely applied measures consists in that perforated plate *1* (Fig. 4.6) is placed in the bulk of boiler water at some distance from the water plane, Δh, with the plate covering the entire evaporating area. The perforated metal plate offers resistance to steam flow and thereby levels off the load carried by the evaporating surface and decreases the extent of boiler water swelling.

4.2.2. Operating Conditions for Drum-Type Boiler Units

The operation of a boiler unit may be accompanied by a change in steam demand, variations in the level of boiler water and steam pressure. In this connection, the nature of the dependence of steam quality on the variation of these parameters acquires great importance.

Steam contamination increases with rising load. The dependence of S_s and D_s is depicted in Fig. 4.7, in which point *a* represents the maximum admissible salt content of saturated steam. Up to point
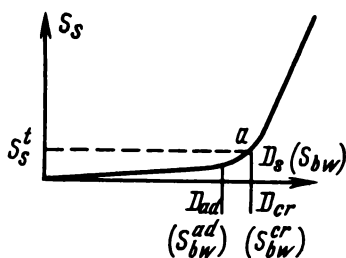
Fig. 4.7. Steam quality versus boiler capacity (versus boiler-water quality)

a steam quality is within admissible limits. The quality of steam deteriorates markedly with a further increase in load. The load above which steam contamination becomes inadmissible by adopted standards is called the *critical load*. Boiler units must be operated under *admissible load* $D_{ad} = (0.7 = 0.8)D_{cr}$ in the region of subcritical loads (the region to the left of point *a*). For this purpose the design capacity of a boiler unit, D_s', must be lower than its

critical load: $D'_s = (0.7\text{-}0.8)D_{cr}$; at $D_{cr} \leqslant D'_s$, the boiler load is limited from steam quality considerations. The magnitude of critical load depends on many factors. It is inversely proportional to boiler water concentration and directly proportional to the height of steam space and efficiency of the steam-water separation devices (boiler internals). So, for a given boiler unit the critical load is not constant and can be raised in a number of ways. The critical load is not amenable to calculations and can only be specified by conducting special thermochemical tests.

In addition to load, the manner in which steam demand varies is also an important factor influencing steam quality. An abrupt increase in steam demand may cause a drop in steam pressure and priming of boiler water, which is accompanied by its swelling and results in a smaller steam space; the latter factor contributes to an increased steam wetness. This explains why it is undesirable to operate boilers under abruptly varying peak loads.

In the course of operation, the actual load carried by a boiler unit can either increase or decrease. Under steady-state conditions, however, the amount of steam produced in a boiler unit is approximately in agreement with the quantity of heat generated in the furnace. Violation of this agreement causes a change in the boiler drum pressure. Operating conditions of this kind arise under a peak load due to abruptly varying rates of steam flows to consumers. Calculations reveal that with a 25 per cent increase in steam demand above the rated steam load, a drum steam pressure of 11.0 MPa drops at a rate of 0.012 MPa/s, and a pressure of 3.5 MPa at about 0.007 MPa/s; this means that high-pressure boiler units are more sensitive to sharp changes in steam demand. When the load increases in such a manner, the level of boiler water rises at a rate of 30 to 50 mm/s and 40 mm/s for high- and medium-pressure drums respectively.

The dependence of steam quality on the boiler water level is similar to the dependence $S_s = \varphi(D_s)$ plotted in Fig. 4.7. It is clear that a maximum (critical) height of boiler water level also exists, above which the quality of steam deteriorates sharply. For a boiler unit in service, an upper and a lower water level are prescribed. The first is taken such as to ensure the generation of high quality steam, and the second to provide reliable circulation. It is good practice to operate boilers with boiler water kept at a middle level without its sharp variations.

4.2.3. Quality of Boiler Water

The quality of steam generated in properly designed and well operated boiler units depends only on the quality of boiler water, $S_s = f(S_{bw})$, as illustrated in Fig. 4.7. Up to point α an increase in the boiler-water salt content tells little on the salt content of steam, which is within the admissible limits, S_s^t, during this stage of operation. A further increase in S_{bw} causes a considerable deterioration of steam quality. The salt content of boiler water at point a is said to be critical. In practical operation, the admissible salt content S_{bw}^{ad} is 20 to 30 per cent lower than the critical. The dependence of the salt content of steam on the salt content of boiler water, $S_s = f(S_{bw})$, is determined by conducting thermochemical tests. This dependence, plotted in Fig. 4.7, is most characteristic for cases of droplet carry-over. The critical salt content of boiler water is not constant for a given boiler unit since it can always be increased by applying a number of measures.

An increase in S_{bw} makes boiler water prone to *foaming*, which leads to the formation of stable foam on the evaporating surface. The appearance of foam in the drum is very objectionable, since disintegrated foam is a source of increased steam wetness. In the event of profuse foam formation, flakes of foam may be entrained into the superheater and cause a high water content of steam and its contamination. Of the various conditions contributing to foaming, the following should be indicated: a high boiler-water salt content; oil present in boiler water or a high alkali concentration; and suspended fine-dispersed sludge in boiler water.

A short-time deterioration of the quality of steam generated in boiler units is observed periodically. This phenomenon has been given the name boiler *priming*. It may be caused by an abrupt drop in drum steam pressure due to increased steam demand, a considerable rise in boiler water level, the penetration into boiler water of oil or alkali in a quantity exceeding the amount stipulated by the standards for boiler water as regards its alkalinity and total solids content. The final result is always a smaller height and volume of the steam space due to a higher boiler-water level, which is just the direct cause of a greater water content of steam.

4.3. Formation of Salt Deposits in Turbines and Superheaters. Removal of Deposits

4.3.1. Steam Turbines

In steam turbines salts settle primarily on blades. This results in rougher blade surfaces, distorted blade-channel profiles and in heat-drop redistribution among turbine stages due to nonuniform deposition of salts in individual stages. The turbine efficiency thus decreases. In the event of considerable deposition of salts on turbine blades and nozzles, the clear passage for steam flow diminishes and the turbine capacity falls off. When merely 0.6 to 0.8 kg of various compounds precipitate in the high-pressure cylinder of a supercritical-pressure turbine rated 300 MW, the consumption of reference fuel increases by 4 to 5 g/kW h.

The formation of deposits in turbines results from intricate processes that proceed in the course of steam flow. The superheated steam entering a turbine always contains a certain amount of nonvolatile substances in the form of dry hard particles and in a dissolved state. At pressures over 7.0 MPa, a large fraction of substances present in superheated steam is found to be in a dissolved state. Steam conditions vary continuously in a turbine, i.e. steam pressure and temperature gradually decrease. The solubility of substances contained in steam also changes. If steam at the turbine inlet has been saturated in respect to a substance, the latter begins to precipitate from the supersaturated steam solution onto the blades of even the first turbine stages. But if the concentration of a given substance in steam is less than the concentration at saturation, precipitation of the substance will occur in the stages where a supersaturated steam solution forms. The dry substances present in steam (or particles in the form of a thick solution) may also settle on blades as they strike and adhere to their surface. The most intensive deposition of soluble compounds is observed at relatively high temperature and pressure of steam. Water-nonsoluble silicic acid deposits appear primarily in the zone of weakly superheated or saturated steam.

The deposits forming in turbines can consist of water-soluble and nonsoluble compounds. The former include sodium compounds (Na_2SO_4, $NaCl$, Na_2SiO_3, $NaOH$), the latter being iron and aluminium oxides and silicic acid. The composition of deposits forming in high- and intermediate-pressure turbines differs greatly.

In intermediate-pressure turbines ($\leqslant 4$ MPa), 70 to 80 per cent of deposits are composed of sodium sulphate, sodium chloride and sodium carbonate, while the main fraction of deposits in high-pressure turbines (4.0 to 10.0 MPa) consists of silicic compounds. Compounds such as CuO, Fe_2O_3, SiO_2 fall out in the superhigh-pressure and high-pressure cylinders of supercritical-pressure turbines; the deposits in intermediate-pressure and low-pressure cylinders mostly contain Na_2SiO_3 and SiO_2, although deposits of Fe_2O_3 are also encountered in these cylinders (Fig. 4.8).
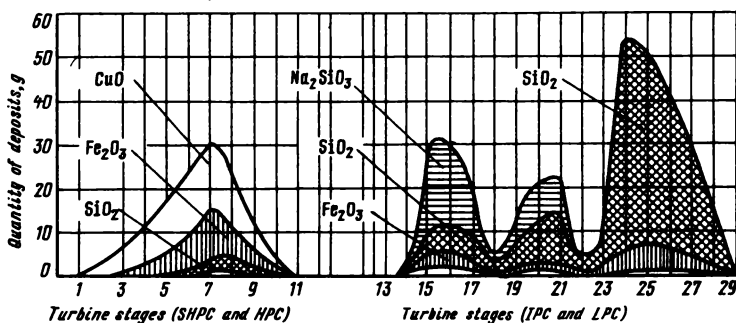

Fig. 4.8. Quantity of deposits in turbine stages and their composition

The main method of controlling depositions in turbines consists in preventing their formation by ensuring the generation of high-quality steam. But if deposits form all the same, they are removed by washing the turbine blading with wet steam. Water-soluble deposits are washed off and removed into the turbine condenser. Such partial washing-off and removal of soluble deposits from turbines are observed during starting and stopping. Washings of turbines with wet steam, particularly supercritical-pressure turbines, are a very responsible task. They are conducted by following a special program and exercising thorough control of the parameters that determine the procedure, with all operations involved well prepared and the equipment adjusted. Deposits poorly soluble in water are removed by injecting into the steam the solvents such as sodium hydrate, ammonium, hydrazine and complexing agents (EDTA). Washing of turbines may be carried out

under a partial load (75-80 per cent of the rated load), under partially cooling conditions and under full load. In the latter case turbine washing must be carried out with utmost care.

4.3.2. Superheaters

The saturated steam leaving a boiler drum passes into a superheater. Here, the droplets of boiler water entrained by the steam evaporate, while a fraction of substances dissolved in the steam is left in the superheater or carried over to the turbine.

A droplet of boiler water will be fully evaporated in the superheater if steam superheat temperature t_{ss} exceeds the boiling temperature of the saturated solution, $t_{s.sol}$. When $t_{s.sol} > t_{ss}$ the droplet cannot evaporate and it may leave the superheater in the form of a thick solution. The numerical value of $t_{s.sol}$ depends on the composition of substances present in the droplet. When substances with a positive solubility coefficient (NaOH, NaCl, KCl) prevail, the condition $t_{s.sol} > t_{ss}$ may become valid. The inequality $t_{s.sol} < t_{ss}$ holds when substances with a negative solubility coefficient (Na_2SO_4, Na_3PO_4) prevail in a droplet of boiler water.

A fraction of substances contained in the droplets of boiler water will dissolve in steam. Inasmuch as the solubility of substances in steam increases with pressure, then in the superheaters of high- and superhigh-pressure boiler units a considerable part of steam-entrained salts will dissolve and pass through the superheaters into the steam mains. Deposits may form in the superheaters of high- and superhigh-pressure boiler units if the steam passing through them is considerably wet. However, these deposits will gradually pass into the steam. In intermediate-pressure boiler units, almost all nonvolatile impurities present in saturated steam fall out in the superheater (if their amount exceeds the admissible quantity). Substances such as Na_2SO_4, Na_2SO_3, Na_3PO_4, Na_2SiO_3 will be the first to precipitate.

Experience indicates that the salt deposits forming to some extent in the superheaters of drum-type boiler units consist as a rule of well water-soluble sodium compounds. Accumulation of deposits is prevented by washing the superheaters. Common and individual washings are distinguished. When a superheater undergoes common washing, water is delivered into the superheated-steam header, from which, via loops (coils), water passes into the drum. If the saturated-steam header of the superheater is fitted with a drain line, the

washing water is drained to waste. Prior to washing, the super-heater is filled with water and is left to stay for 1 to 2 hours.

The advantage of common washing consists in that it is quite practicable, takes little time and labour. But it cannot ensure the removal of deposits from all the loops of a superheater. Individual washing, in the course of which each coil is washed individually, is free of this demerit, though it takes considerably more time. That is why common washing is usually carried out when a boiler unit is laid up for preventive maintenance, and individual washing is undertaken during major repairs.

The foregoing pertains mainly to boiler units of a steam pressure up to 4.0 MPa. Washing of modern drum-type boiler units rated 15.5 MPa is a rather intricate and difficult operation. Con-tamination of the superheaters of boiler units of this kind is prevented by ensuring proper steam-water separation in boiler drums, i. e. by generating high-quality saturated steam.

4.4. Separation Devices

The drums of modern boiler units are fitted with various devices, the so-called drum internals, whose objective is to ensure purity of saturated steam; they are designed to quench the kinetic energy of steam-water mixture streams entering the drum, to separate steam from water (coarse separation) and to dry the steam, i. e. to remove water droplets from it (fine separation).

Separation of water from steam is based on the difference between the densities of saturated steam, ρ'', and water, ρ': the greater the difference, the easier the moisture is separated.

The difference $\rho' - \rho''$ decreases with rising steam pressure, so that the process of separation becomes more involved. This difference in densities is used in practice in a number of ways, the main of which consists in a uniform distribution of steam in the free steam space of the drum to ensure the lowest possible steam velocities in the drum. This creates favourable conditions for the moisture droplets to settle on the evaporating surface (settling separation). Another approach is to place deflecting metal baffles on the path of the steam flow. As they strike the baffle, the droplets adhere to its surface. The steam then changes its direction of motion and the remaining particles·are thrown out of the flow by centrifugal force.

The first stage of separation involves quenching the kinetic

energy of the steam-water flows as they enter the boiler drum at high velocities and separating the main mass of water from the steam. These two processes usually combine. As the mixture enters the steam space of the drum, the kinetic energy of the stream is quenched by means of baffles and slotted or solid partitions.

When the steam-water mixture is introduced into the water space of a boiler drum, its kinetic energy is quenched in the layer of boiler water. In this case uniform distribution of the separated steam over the entire evaporating surface must be ensured to preclude the appearance of local high-velocity steam flows. Such distribution is provided by means of perforated plates placed in the
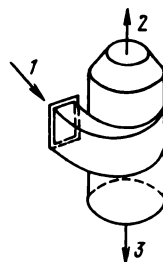

Fig. 4.9. Cyclone steam-water separator

1 — inlet of steam-water mixture; 2 — steam outlet; 3 — water outlet

boiler water (see Fig. 4.6). A perforated plate offers a certain resistance to the flow of steam, so that it spreads uniformly over the entire plate surface. In addition to baffles, cyclone steam-water separators find most effective use, especially in the case of concentrated boiler water liable to foaming. A cyclone steam-water separator (Fig. 4.9) is a hollow cylinder. A special duct delivers a steam-water mixture into the cylinder tangent to its walls in order to impart rotational motion to the flow. The water is thrown by centrifugal force to the walls, flows down, and steam goes upward along the generating line in the centre of the cylinder. In this way impactless quenching of the kinetic energy of the steam-water flow takes place, which precludes breaking of water. However, cyclone steam-water separators offer increased resistance to fluid flow and thus they cannot be used where the circulating head is insufficient.

The main element of all modern steam-separation circuits is the large free vapour space. ensuring settling separation. Various steam-water separating drum internals in use today permit

generation of high-quality steam only if they are properly and carefully assembled and matched in situ.

The main requirement imposed on the erection and assembly of steam-water separating devices is that high-velocity boiler water, feed-water, steam water and wet steam flows must not come into contact with the flow of dried steam, by-passing the water-separating drum internals and the separation-active free space.

Steam-water separating devices are incapable of removing substances dissolved in steam. For this, in addition to the separating devices, boiler drums are fitted with means to secure steam washing with feedwater or condensate. The washing principle is based on that saturated steam is brought into contact with feedwater or condensate of higher purity than boiler water to enable a considerable part of particles dissolved in steam to pass into wash water. Steam washing is carried out with the aid of a bubbler by blowing the steam through a layer of wash water and then transferring it to steam-water separating drum internals.

4.5. Blowdown of Natural-Circulation Boilers

Blowdown is defined as the removal from a boiler unit of a fraction of the boiler water and its replacement by feedwater. This is done to prevent an excessive concentration of undesirable substances in boiler water. *Continuous* and *intermittent* types of blowdown are distinguished. The objective of continuous blowdown is to maintain a definite concentration of substances in boiler water. Intermittent blowdown is aimed at removing sludge from a boiler unit.

Blowdown is used to set up and maintain a salt balance for boiler water, i.e. to keep the amount of salts entering a boiler unit with feedwater equal to that removed by blowdown. Let us consider the quantitative aspect of the salt balance. A boiler unit with a rate of feedwater flow equal to D_{fw}, t/h, receives in an hour salts in the amount of $S_{fw}D_{fw}$. During the same period of time, steam and blowdown water carry away salts in the amount of S_sD_s, g, and $S_{bw}D_{bd}$, g, respectively. Under-steady state operating conditions the following equality must be satisfied:

$$S_{fw}D_{fw} = S_sD_s + S_{bw}D_{bd} \qquad (4.7)$$

The notations S_{fw}, S_{bw} and S_s in formula (4.7) denote not only

the salt content, but also the concentration of any substance (for instance silica) in feedwater, boiler water, and steam, respectively. This concentration is then used in calculations to determine the rate of blowdown. Substituting into equation (4.7) $D_{fw} = D_s + D_{bd}$ and solving the equation for D_{bd}, we find

$$D_{bd} = \frac{S_{fw} - S_s}{S_{bw} - S_{fw}} D_s \tag{4.8}$$

whence blowdown in per cent

$$p_s = \frac{D_{bd}}{D_s} 100 = \frac{S_{fw} - S_s}{S_{bw} - S_{fw}} 100 \tag{4.8a}$$

Substituting into Eq. (4.7) $D_s = D_{fw} - D_{bd}$, we obtain another expression for percentage blowdown

$$p_w = \frac{D_{bd}}{D_{fw}} 100 = \frac{S_{fw} - S_s}{S_{bw} - S_s} 100 \tag{4.9}$$

Formulae (4.8a) and (4.9) can be simplified assuming $S_s = 0$:

$$\left.\begin{aligned} p_s &= \frac{S_{fw}}{S_{bw} - S_{fw}} 100 \\ p_w &= \frac{S_{fw}}{S_{bw}} 100 \end{aligned}\right\} \tag{4.10}$$

This simplification is admissible when the numerical value of S_{fw} exceeds considerably the value of S_s. If S_{fw} is small and comparable to S_s, as is the case where condensate is used as feedwater for boiler units, formula (4.8a) may yield too low results. Under such conditions, it is necessary to take into account the concentration of the reagents introduced into the drum of a boiler unit.

For newly designed boiler units, the quality of boiler water is unknown, and the foregoing formulae prove of little help in determining the amount of blowdown. In this case use is made of the formula

$$p_s = \frac{\sum L_t S_{ch}}{S_{bw} - (1 - \beta) S_{ch}} \tag{4.11}$$

where $\sum L_t$ = total loss of condensate, %

   β = fraction of steam separated in the blowdown flash tank

   S_{ch} = salt content of chemically treated water

The concentrations of substances in feedwater and boiler water are interrelated and can be specified by the formula

$$S_{fw} = \frac{p_s}{100 + p_s} S_{bw} \tag{4.12}$$

If α_{ch} fractions of chemically treated water with a salt content S_{ch}, mg/kg (or mg-equiv/kg), are added to feedwater, then it may be assumed with sufficient accuracy that $S_{fw} = \alpha_{ch} S_{ch}$. Substituting this value of S_{fw} into formula (4.11), we obtain the expression relating the quality of chemically treated water to that of boiler water:

$$S_{ch} = \frac{p_s}{100 + p_s} \frac{S_{bw}}{\alpha_{ch}} \tag{4.13}$$

Formula (4.13) is often used in designing water-treatment plants.

In practice, water control of a boiler unit is often restricted to observing one of the following boiler water quality characteristics: alkalinity, salt content, silica content. The limiting characteristic is taken to be the one which necessitates a greater amount of blowdown. Soviet maintenance rules for electric power stations prescribe the following amounts of blowdown: not over 1.0 per cent and less than 0.5 per cent for power plants where distillate or demineralized water is used as makeup water; not over 3 and not less than 0.5 per cent where chemically treated water is used as makeup; and up to 5 per cent if losses of condensate are considerable. Where the calculated or actual amount of blowdown is in excess of the above values, special measures should be taken to keep to the standards.

Continuous blowdown of a boiler unit can be ensured by using a number of layouts, of which the one illustrated in Fig. 4.10 finds most extensive application. Vital components of the layout are the flow meter and the blowdown control unit. The amount of blowdown is abjusted by means of a needle valve and controlled by the readings of the flow meter.

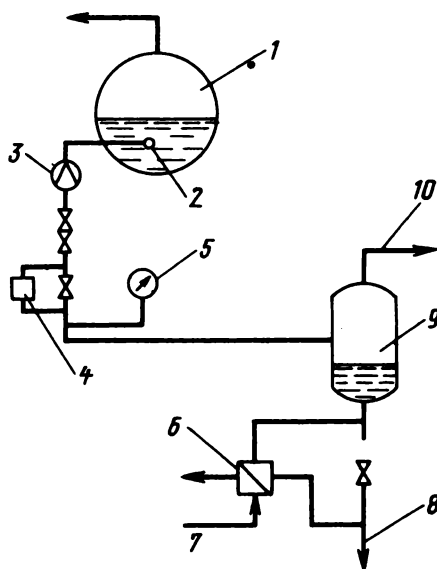The pressure maintained in the blowdown flash tank is to be

Fig. 4.10. Continuous-blowdown hookup

1 — drum; *2* — water inlet device; *3* — flow meter; *4* — needle valve; *5* — pressure gauge; *6* — heat exchanger; *7* — heated water; *8* — drain; *9* — flash tank; *10* — vent (vapour)

considerably lower than the boiler pressure. The fraction of boiler water, β, per cent, that evaporates in the flash tank by virtue of this pressure difference can be calculated by the formula

$$\beta = \frac{i_{bw} - i_{sw}}{i_s - i_{sw}} 100 \tag{4.14}$$

where i_{bw}, i_{sw}, and i_s represent respectively the heat contents (enthalpy) of boiler water, water separated in the flash tank, and of the steam obtained in the flash tank, J/kg.

Flash steam is usually delivered to a deaerator, but may be used to cover other needs. The separated water is directed to a heat exchanger where it gives up heat to chemically treated or initial water to be treated. Continuous blowdown water can be used as makeup in heat-distribution systems, as feed for evaporators, etc.

Along with continuous blowdown, intermittent blowdown is also

practiced to remove sludge that usually accumulates at bottom points — in lower drums, mud drums, waterwall headers. The requirements for intermittent blowdown depend on the sludge content of boiler water.

4.6. Removal of Impurities from a Steam-Water Cycle (Cycle Cleanup).

The sources of substances that continuously enter the feed system of boiler units may be traced to leakage of cooling water in turbine condensers, makeup water, and processes of corrosion. To prevent accumulation of nonvolatile substances in the steam-water cycle that disturb its performance, one should systematically remove a certain amount of these impurities. Blowdown of drum-type boiler units copes with this problem adequately. But it can only be used in boiler units operated under subcritical steam conditions, in which case the impurities can concentrate in the zones from where blowdown is undertaken, i.e. when the distribution coefficient (Sec. 4.1) of these impurities is rather small. This makes blowdown effective.

Blowdown is of no use for subcritical and supercritical-pressure once-through boiler units, and the main way of removing ionic and suspended impurities is the treatment of a fraction of the entire volume of feedwater in special (polishing) demineralizing plants. This is the reason why high-power boiler-turbine units are fitted with individual demineralizing plants.

4.7. Stage Evaporation

The essence of stage evaporation is based on the following. The quality of steam depends on the concentration of substances in boiler water with which steam is in contact before it enters the steam space of the boiler unit. Since K'_d (see Sec. 4.1) for a given boiler in steady-state conditions is almost constant, S_s can be diminished only by reducing impurity concentration S_{bw} in boiler water, which can be done in a number of different ways. To find out which of the methods is most expedient, let us consider balance equation (4.7) for nonvolatile substances present in a boiler unit. Disregarding S_s, we can write

$$S_{bw} = \frac{S_{fw}D_{fw}}{D_{bd}} \tag{4.15}$$

or, substituting S_{bw} into equality (4.1),

$$S_s = \frac{S_{fw}D_{fw}}{D_{bd}}K_d^t \qquad (4.16)$$

It is clear from Eq. (4.16) that S_s can be kept to a minimum either by reducing the concentration of substances in feedwater, S_{fw}, or by increasing the rate of blowdown. It is inadmissible to reduce D_{fw} since this is equivalent to diminishing the load carried by a boiler unit. A decrease in S_{fw} can be ensured in two ways: by demineralizing makeup water or by decreasing the amount of chemically treated water used as makeup for the feed system.

Demineralizing cannot so far be used in all cases. A reduction in the amount of makeup water entails the need for a greater fraction of condensate or distillate in feedwater, which proves impossible to satisfy in many instances. In practice, S_s is usually decreased by increasing the amount of blowdown taken from a boiler unit. However, for ordinary boiler units not fitted with means for stage evaporation, the amount of blowdown is restricted to about 5 per cent since the operations involved often lead to inadmissibly high heat losses.

A reduction of S_{bw} at the expense of greater values of D_{bd} becomes possible and suitable in boilers operated with stage evaporation. Figure 4.11 shows the water-flow circuits of an ordinary boiler unit and of a two-stage evaporation boiler unit. The latter has two independent water-flow circuits whose water spaces are in free communication only through hole *1* provided in drum partition plate *2*. Feedwater flows into the large section, called the *primary section* or *stage*. The blowdown water from the primary stage serves as feedwater for the *secondary stage* of evaporation, also referred to as the *saline section*. Boiler blowdown is taken only from the saline sections.

In this way stage evaporation is based on the creation of different salt concentrations of boiler water in the water-flow circuits forming the primary and secondary (saline) sections. The distinguishing feature of stage evaporation is that the greatest fraction of steam is generated from the boiler water filling the primary section, which has a considerably lesser salt content than the blowdown water. From this it follows that the quality of boiler water in the primary section is the main characteristic by which one can judge of the water control applied to the boiler unit.

The secondary stage of evaporation (whose steaming capacity is

usually expressed as a percentage of D_s and denoted by n) generates the steam of the same quality as a boiler unit operated without stage operation provided they have the same values of p_s and S_{fw}. However, inasmuch as the amount of steam produced by the primary stage is $(100 - n)/n$ times greater than the quantity of steam obtained from the secondary section, the quality of steam
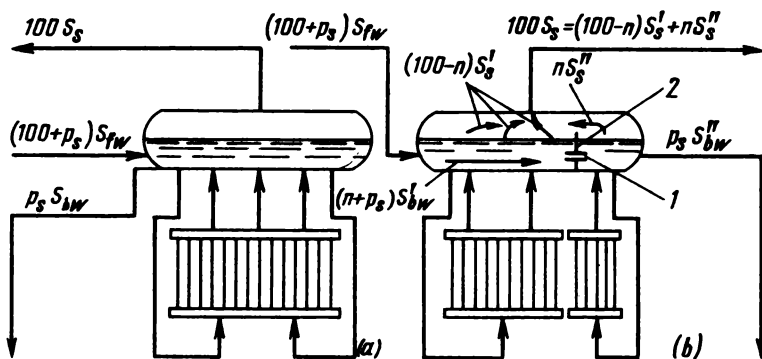

Fig. 4.11. Water-flow circuits in boiler units operated without stage evaporation (a) and with two-stage evaporation (b)

generated in the boiler unit with two-stage evaporation is higher than the quality of steam generated in the single-stage unit under otherwise identical conditions. This property of stage evaporation is of great value when feedwater of poorer quality is to be used in boiler units.

It is convenient to consider the relationships presented below by assuming the steaming capacity of a boiler unit to be equal to 100 t/h. In this case the numerical values of p_s and n can be expressed both in per cent and in t/h. The quantities pertaining to the primary section, secondary section, and to the boiler unit as a whole will be marked respectively with one prime, two primes, and without primes. For a boiler unit fitted with drum internals for two-stage evaporation, we can write the following balance equations for impurities:

for the boiler unit as a whole

$$(100 + p_s)S_{fw} = 100S_s + p_sS_{bw} \qquad (4.17)$$

for the primary section

$$(100 + p_s)S_{fw} = (100 - n)S'_s + (n + p_s)S'_{bw} \qquad (4.18)$$

Substituting $S'_s = K'_d S'_{bw}$, we obtain

$$(100 + p_s)S_{fw} = (100 - n)K'_d S'_{bw} + (n + p_s)S'_{bw}$$

whence

$$S'_{bw} = \frac{(100 + p_s)S_{fw}}{n + p_s + (100 - n)K'_d}$$

Since the quantity $(100 - n)K'_d$ is rather small compared to $n + p_s$, it can be ignored. Then

$$S'_{bw} = \frac{100 + p_s}{n + p_s}S_{fw} \qquad (4.19)$$

For the secondary section,

$$(n + p_s)S'_{bw} = nS''_s + p_s S''_{bw}$$

Since $S''_s = K''_d S''_{bw}$, then

$$(n + p_s)S'_{bw} = (nK''_d + p_s)S''_{bw}$$

whence

$$S''_{bw} = \frac{n + p_s}{nK''_d + p_s} S'_{bw} \qquad (4.20)$$

At small values of K''_d and n, the product nK''_d can be disregarded, then

$$S''_{bw} = \frac{n + p_s}{p_s} S'_{bw}$$

The balance equation for impurities contained in steam is

$$100S_s = (100 - n)S'_s + nS''_s$$

whence

$$S_s = \left(1 - \frac{n}{100}\right)S'_s + \frac{n}{100}S''_s \qquad (4.21)$$

The efficiency of stage-evaporation circuits is usually estimated by the ratio of the total solids (alkalinity, silica content) of boiler water in the last stage of evaporation to that in the primary stage. For instance, for a two-stage evaporation circuit, the ratio

$$K_c = S''_{bw}/S'_{bw} \qquad (4.22)$$

This ratio is called the rate of concentrations.

The higher the value of K_c, the more efficient the two-stage evaporation layout. In practice, K_c is usually kept at 3 to 10. At $K_c > 10$, the concentration of impurities in the saline section can become so high that they may cause a deposition hazard. Expression (4.20) yields

$$K_c = \frac{n + p_s}{n K''_d + p_s}$$

whence

$$n = \frac{K_c - 1}{1 - K_c K''_d} p_s \qquad (4.23)$$

The product $K_c K'_d$ does not exceed 0.08 to 0.1, therefore it may be ignored in a number of cases. Thus, it is safe to assume that

$$n = (K_c - 1) p_s \qquad (4.24)$$

The sections of a stage evaporation hookup can be arranged both inside and outside a boiler drum. Inside the drum, the secondary sections are commonly located at the ends of the drum, as illustrated in Fig. 4.12. The demerit of such an arrangement is that blowdown has to be taken from two points in the drum, making chemical water control more involved. Another shortcoming of this arrangement is that boiler water can be forced to flow from the secondary into the primary sections over the partitions. Water overflow is considerably reduced in stage-separation outfits with secondary sections mounted outside the drum.

Cyclone steam-water separators 2 are mounted next to drum 1 (Fig. 4.13). Waterwall surfaces 3 (usually a part of side waterwalls) are connected to these cyclones. Feedwater 4 flows into the drum (primary section), from which feed of the cyclones is effected. The cyclones and the waterwalls connected to them form independent

Fig. 4.12. Arrangement of secondary evaporation stages at ends of a boiler drum
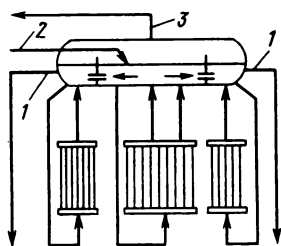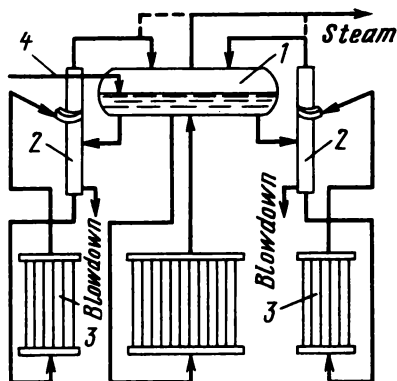*1* – blowdown: *2* – feedwater: *3* – steam

Fig. 4.13. Two-stage evaporation lay out with cyclone steam-water separators mounted outside

water-flow circuits. From the cyclone steam-water separator, the steam is directed into the drum or just into a superheater if the steam quality is sufficiently high. Blowdown is taken from the cyclones. The layout with outside-mounted cyclone steam-water separators permits partial unloading of the drum's steam space and thus contributes to steam quality. In the event of three-stage evaporation, two sections are arranged inside the boiler drum, while the outside-mounted cyclone steam-water separators form the third section.

Let us consider a numerical example for a boiler unit for which the quantities characterizing boiler performance have the following values: $D_s = 100$ t/h, $D_{bd} = 5$ t/h, $n = 20$ per cent, $S_{fw} = 200$ mg/kg, $K_d^t = 0.02$ per cent, $p = 3.5$ MPa. The value of S_s should not exceed 0.3 mg/kg. First, let us determine the quality of steam generated in the boiler unit without stage evaporation,

making use of formula (4.16). We find that

$$S_s = \frac{2 \times 10^{-4} \times 200 \times 105}{5} = 0.84 \text{ mg/kg}$$

The salinity (salt content) of steam is too high. The required steam quality with a salt content of 0.3 mg/kg can be ensured only at a steaming capacity

$$D_s = D_{fw} - D_{bd} = \frac{D_{bd}S_s}{K'_d \cdot 200} - D_{bd} = \frac{5 \times 0.3}{2 \times 10^{-4} \times 200} - 5 \approx$$

$$\approx 32.5 \text{ t/h}$$

Inasmuch as S_{fw} cannot be reduced due to the lack of condensate, the most satisfactory decision to be taken here is to tailor the boiler unit for two-stage evaporation. Then, we shall have

$$S'_{bw} = \frac{105}{25}200 = 840 \text{ mg/kg} \quad \text{and} \quad S'_s = K'_d S_{bw} = 2 \times 10^{-4}$$
$$\times 840$$

$$= 0.168 \text{ mg/kg}$$

$$S''_{bw} = \frac{25}{5}840 = 4200 \text{ mg/kg and}$$

$$S''_s = K'_d S''_{sw} = 2 \times 10^{-4} \times 4200 = 0.84 \text{ mg/kg}$$

Steam quality

$$S_s = 0.8 \times 0.168 + 0.2 \times 0.84 = 0.3 \text{ mg/kg}$$

Thus two-stage evaporation allows us to do away with the limits set on boiler load from considerations of steam quality.

Review Questions

1. What factors affect the quality of steam generated in drum-type boiler units?

2. The quality of steam generated in a drum-type boiler unit out of repair has become worse than it was prior to repair. Name the causes that might be responsible for steam deterioration.

3. What factors determine the quality of steam generated in supercritical-pressure once-through boiler units? What harmful substances contaminate the steam?

4. What is the essence of stage evaporation?

5. What are the consequences of salt deposition on turbine blading?

6. A short-time 60-per cent drop in turbogenerator load took place. The power rating of the turbogenerator is 100 MW. The electric conductivity of turbine condensate increased considerably over the period between the drop in load and its subsequent increase to the rated level. Explain this phenomenon.

7. What are the methods of pure steam generation?

Corrosion of Heat-Power Equipment. Control of Corrosion

5.1. The Essence and Forms of Corrosion of Metals

Corrosion of metals is their destruction under the action of surrounding media (water, steam, furnace gas in power engineering) as a result of chemical and electrical processes that take place on the surface of metals. The destruction of the surface of metal caused by mechanical processes (friction, impact) is referred to as *erosion*.

Corrosion manifests itself in different forms. *Uniform* and *nonuniform*, or *local*, forms of corrosion are distinguished. Uniform (general) corrosion is characterized by the destruction of metal over the entire surface (blanket or surface corrosion). Nonuniform corrosion is classified as *spot-*, *honeycomb-*, *point*, *selective* and *intercrystalline*. In the event of honeycomb corrosion, the metal is deeply destroyed, and the more so when point corrosion takes place. This is the most undesirable kind of corrosion since even an insignificant loss of metal may result in failure of equipment. With selective corrosion, only one of the components of an alloy is affected: for instance, in brass (copper-and-zinc alloy) only zinc dissolves. This kind of corrosion most commonly occurs in turbine condensers where brass tubes experience dezincification on exposure to mineralized or sea water used for cooling purposes. With zinc so removed, brass becomes brittle.

Chemical corrosion arises due to purely chemical processes and occurs subsequent to direct interaction between metal and surrounding without generation of electric current. Here corrosion products form directly on surface sections where the reaction takes place. An example of this kind of corrosion is the oxidation of metal by water vapour at temperatures of 623-773 K and higher

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$
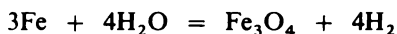
Electrochemical corrosion is most frequently encountered at electric power stations. It originates when metal is attacked by electrolytic solutions and is characterized by the flow of current from one part of metal to another. To elucidate the essence of electrochemical corrosion, let us consider a conventional copper-zinc cell (Fig. 5.1). In the cell, zinc and copper plates are
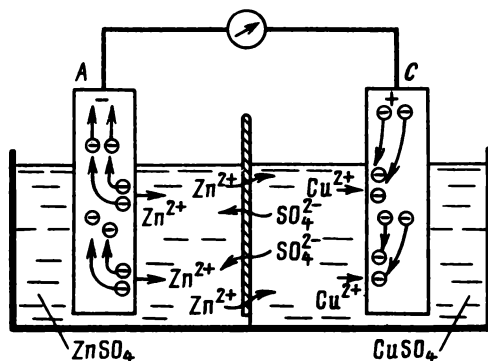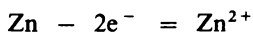

Fig. 5.1. Schematic diagram of a copper-zinc galvanic cell

immersed in solutions of $ZnSO_4$ and $CuSO_4$ respectively. Here it is the zinc plate that is subjected to corrosion. Zinc passes into the solution in the form of ions, leaving free electrons in the plate (this is an *anodic* process)

$$Zn - 2e^- = Zn^{2+}$$

If we connect the two plates (electrodes) by a metal conductor, the free electrons will move from the zinc (anode) to the copper plate (cathode) where they will be bound by the copper ions that are being reduced in the process and settle on the copper plate (this is *a cathodic* process):

$$Cu^{2+} + 2e^- = Cu$$

The anodic and cathodic processes are supplemented by the transfer of electrons from the anode to the cathode and by the motion of ions in the electrolyte — anions move to the anode and cations to the cathode. Thus, a chemical reaction proceeds in the

element, resulting in that the zinc gives up electrons (oxidizing reaction — anodic process), and the copper ions receive them (reducing reaction — cathodic process):

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$
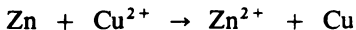
The number of electrons travelling from the anode to the cathode (i. e. current I) is proportional to the number of zinc ions that pass into the solution; the greater the current, the more intensive is corrosion. Since

$$I = (V_c - V_a)/R$$

(where V_a, V_c are the anode and cathode potentials, respectively), then the intensity, or rate, of corrosion is determined to a great extent by the electrode potential difference $V_c - V_a$ (the anode is more negative than the cathode) at a given value of R. Experience shows that the difference $V_c - V_a$ is considerable in the initial period of cell operation and then diminishes to some value with time. A decrease in the difference between the electrode potentials that leads to a smaller rate of corrosion results from *polarization*.

The electrode process which reduces polarization, i. e. intensifies corrosion, is known as *depolarization*. The substances that contribute to depolarization are called *depolarizers*. It follows that for initiation and progression of corrosion, the electrolyte must contain depolarizers, i. e. substances capable of binding free electrons. When $V_c = V_a$, electrochemical corrosion ceases, which is indicative of complete electrochemical homogeneity of the metal surface, i. e. the absence of a galvanic couple. Corrosion also ceases when $R \rightarrow \infty$, which points to the absence of electrolyte, called the conductor of the second kind.

Thus for electrochemical corrosion to originate and proceed, the following elements must exist: a galvanic couple, i.e. two metallic portions with different potentials, electrolyte in contact with the electrodes of the couple, and depolarizers. Elimination of one of these elements makes electrochemical corrosion impossible. This type of corrosion control finds wide practical application.

The formation of galvanic couples in metal, in the wall of a steel tube, for instance, is due to the electrochemical heterogeneity of various sections of the surface. If the potentials at some sections become more negative than the potentials at other sections due to a number of reasons, the above considered processes originate and lead to the destruction of anode sections (Fig. 5.2).

The protection of metal against corrosion essentially reduces to maintaining intact the protective oxide film that always forms on its surface. That is why the factors responsible for splitting or destruction of the oxide film simultaneously give rise to corrosion.
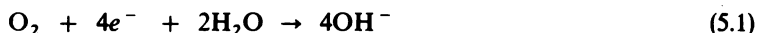
At electric power stations, water-dissolved oxygen usually takes the part of depolarizers for the cathode sections of surfaces (oxygen

Fig. 5.2. Electrochemical corrosion of metal

1 — tube wall; *A* — anode section; *C* — cathode section

depolarization):

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \tag{5.1}$$
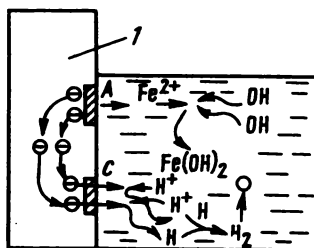
or hydrogen ions' (hydrogen depolarization)

$$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2 \tag{5.2}$$

Experience shows that ferric oxide, Fe_2O_3, and nitrites, i.e. nitrous acid salts, $NaNO_2$, can also act as depolarizers. Of the three iron oxides, FeO, Fe_2O_3 and Fe_3O_4, only FeO and Fe_3O_4 can be in equilibrium with Fe. At a temperature of 843 K and above, the reaction
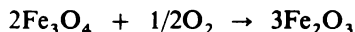
$$Fe_3O_4 + Fe \rightarrow 4FeO$$

takes place, which proceeds in the reverse direction as the temperature decreases.

When ferric oxide, Fe_2O_3, comes into contact with iron, the latter oxidizes by the formula

$$4Fe_2O_3 + Fe \rightarrow 3Fe_3O_4$$

When Fe_3O_4 is exposed to water, oxygen-enriched magnetite turns again into Fe_2O_3:
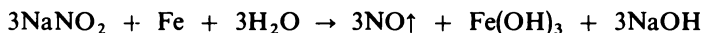
$$2Fe_3O_4 + 1/2O_2 \rightarrow 3Fe_2O_3$$

These two processes of mutual iron oxide conversion, accompanied by a change of valency, can under some conditions lead to (and actually cause) honeycomb corrosion.

The most probable course of nitrite corrosion can be described by the following reaction:

$$NO_2^- + e^- + H_2O \rightarrow NO\uparrow + 2OH^-$$

or

$$3NaNO_2 + Fe + 3H_2O \rightarrow 3NO\uparrow + Fe(OH)_3 + 3NaOH$$
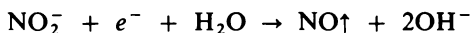
Nitrites appear in water due to nitrifying bacteria that oxidize ammonium to NO_2^- or NO_3^-. These bacteria may settle in pipelines and mechanical filters and add to the concentration of nitrites in the water-treatment cycle. This phenomenon is controlled by periodical chlorine treatment of bacteria-infected pipelines and apparatus.

## 5.2.   Main External Factors Promoting Corrosion

The development of electrochemical corrosion depends on many factors that can be subdivided into two groups: internal factors (the grade and kind of metal, its cleanness, the presence of stresses, mechanical or heat treatment, etc.) and external factors of corrosion (nature of the surrounding medium, pH value, etc.).

Under operating conditions of heat-power equipment, the main factor determining the intensity of corrosion is water-dissolved oxygen. Since oxygen is a depolarizer, it effectively contributes to the action of other factors of corrosion. Oxygen corrosion of metal results first in the formation of ferrous hydroxyde

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

Corrosion with the participation of oxygen in a neutral or alkaline medium leads to the formation of pits, i.e. to sharply pronounced local destruction of metal. Corrosion products are larger in volume than the iron from which they form, and therefore the outgrowths over the pits appear, which are an indication of honeycomb corrosion. At $pH < 7$, oxygen corrosion usually develops more evenly. Oxygen gets into water from the air. So, care must be taken to preclude exposure of deaerated water or condensate to the atmosphere.

The other important factor influencing the development of corrosion is the presence of carbon dioxide, CO_2, in water. When dissolved in water, carbon dioxide forms carbonic acid, H_2CO_3, that dissociates to form hydrogen ions:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad (5.2a)$$
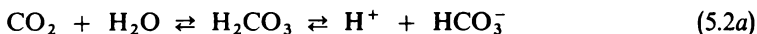
The H^+ ions acidify water and cause corrosion attended with hydrogen depolarization (see Sec. 5.1). One must, however, differentiate the conditions in which reaction (5.2a) takes place. If the reaction proceeds in condensate (distillate), i. e. in a medium free or almost free of HCO_3^- ions, even a small amount of dissolved carbon dioxide can reduce considerably the pH value. For instance, the presence of only 0.3 mg/kg of CO_2 in water reduces the pH value to 6. On the contrary, the presence of HCO_3^- in water (natural waters, softened water, i. e. a buffer medium) ensures binding of hydrogen ions — reaction (5.2a) proceeds from the right leftward so that the pH value is held practically constant. That is why carbon-dioxide corrosion is most likely to occur in condensate lines, condensate tanks, air heaters and other similar equipment in which internal surfaces are exposed to condensate.

Characteristic of carbon-dioxide corrosion is that reaction (5.2a) does not proceed rightward to the very end. For this reason H_2CO_3 is also present in water along with H^+ and HCO_3^-. As neutralization of hydrogen ions on the cathode continues, the equilibrium of the reaction is disturbed and it again proceeds from the left to the right, resulting in the appearance of new ions, H^+, which maintain the corrosive aggressiveness of the solution at the former level. This process, which makes up for the decrease in the number of hydrogen ions, goes on until carbonic acid fully dissociates. When a strong acid such as HCl is used for water acidification (pH value being kept the same as with CO_2), the process of this kind does not take place. Here, complete dissociation of HCl into ions is observed and the decrease in H^+ is not compensated for as the process of corrosion develops. For this reason the concentration of H^+ decreases gradually and, hence, corrosion slows down. This also suggests that a CO_2 solution is more aggressive than a HCl solution at the same pH value.

Ions, HCO_3^-, are bound by ions, Fe^{2+}, which originate in the course of steel corrosion. Under some conditions ferrous bicarbonate decomposes with the formation (and deposition) of

ferrous hydroxide and free CO_2:

$$Fe(HCO_3)_2 \rightleftarrows Fe(OH)_2 + 2CO_2$$

CO_2 is now able to react again. But such a process is possible only if water contains a sufficient amount of oxygen required for oxidizing Fe^{2+} into Fe^{3+} and eliminating it from the reaction:

$$2Fe(OH)_2 \rightarrow 1/2O_2 + H_2O \rightarrow 2Fe(OH)_3\downarrow$$
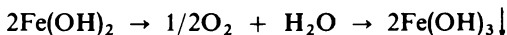
Almost the same conditions may appear in closed-circuit type water-supply systems where acidification is practiced (see Sec. 3.6).

If the corrosion products strongly adhere to the surface of the metal undergoing corrosion and form a sufficiently dense layer, they may greatly reduce the intensity of corrosion or terminate corrosion altogether. The corrosion products act then as a corrosion-resistant coating, isolating the metal from the attacking medium and preventing penetration of depolarizers to the metal. In the presence of CO_2, corrosion products adhere weakly to the surface of metal (they are separated from the metal by the gaseous H_2 being produced) and thus are carried over into boiler units.

5.3. Corrosion of the Water-Condensate Circuit of Electric Power Stations and Industrial Boiler Houses

At electric power stations, corrosion occurs in feed lines, steel water economizers, regenerative feedwater heaters and heat exchangers, and in return condensate lines. The section of the feed line from the deaerator to the boiler drum is always filled with fresh hot water. It comes into contact with the metal that is commonly free of deposits. These conditions contribute to corrosion if water contains depolarizers. Temperature speeds up corrosion, the intensity of which depends on whether oxygen-containing water is heated in a closed heat exchanger or in a tank open to the atmosphere (open circuit, Fig. 5.3). In the first case the rate of corrosion increases continuously with rising water temperature. In open systems the rate of corrosion is maximum at 348-358 K.

Heaters and evaporators usually suffer corrosion on the side of heating steam. Corrosion is caused primarily by dissolved CO_2 contained in condensate.

.As heating steam condenses in a heater, a certain fraction of gases contained in it passes into the aqueous solution. The higher the partial pressure of the gases and the lower the condensate temperature compared with the saturation temperature at that pressure, the larger is the fraction of these gases. Enrichment of the condensate with gases (CO_2, O_2) is more probable when gases are not vented or insufficiently vented from the steam space of heaters.
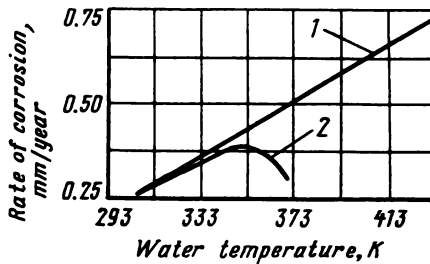
Fig. 5.3. Rate of corrosion versus temperature

1 -- closed system; *2* — open system

The level of condensate is also of importance: if the level is high and a part of the surface of tubes happens to be immersed in the condensate, then the condensate temperature becomes lower than the saturation temperature. This phenomenon is known as subcooling of the condensate. Subcooling increases the solubility of gases in condensate, including the CO_2 gas.

Gases that fail to condense in turbine condensers are evacuated by means of ejectors. Nevertheless, a fraction of CO_2 passes into the condensate and reduces its pH value. If subcooling of condensate takes place and the content of CO_2 in the steam exhausted into a condenser is high, the concentration of carbon dioxide may happen to be high enough to cause corrosion of condensate lines.

Carbon dioxide finds its way into the steam-water circuit of a heat power plant with chemically treated water and due to cooling water leakage in turbine condensers. In both cases, the ions, HCO_3^- and CO_3^{2-}, introduced into the system decompose in the boiler unit, forming CO_2. The most harmful effect of carbon

dioxide corrosion is the contamination of feedwater with iron oxides. Such contamination grows with feedwater temperature and the time of metal exposure to condensate enriched with CO_2.

Methods of controlling corrosion of the feedwater and steam condensate lines of a power station are based on the removal of aggressive gases — oxygen and carbon dioxide — from feedwater and condensate.

The removal of O_2 from water will be considered in detail in Chapter 6. Carbon-dioxide corrosion can largely be prevented by carrying out the following measures:

(1) reducing the amount of free carbon dioxide in steam by appropriate methods of makeup water treatment;

(2) properly removing heating-steam condensate from regenerative feedwater heaters;

(3) completely venting noncondensing gases from the steam space of heaters;

(4) treating feedwater with ammonium or steam with film-forming amines.

Tanks (for chemically treated water, drain-, bottom points-, and condensate tanks) are the sources of water and condensate contamination with iron and oxygen if they are open and not protected against corrosion. The number of such tanks at an electric power station should be reduced to a minimum. They must be given a corrosion-resistant coating and be airtight, i. e. isolated from the atmosphere. This is ensured most efficiently by connecting tanks to the steam volume of atmospheric-pressure deaerators or continuous-blowdown flash tanks, provided the tanks are designed for a corresponding pressure.

Carbon dioxide contained in condensate is bound completely by introducing ammonia into feedwater. In the boiler unit, ammonia passes into the generated steam, and when the latter condenses in heaters or turbine condensers, ammonia dissolves again and increases the pH value of condensate. If condensate contains CO_2, the latter is bound by ammonia following the reaction
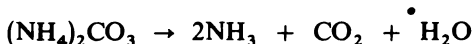
$$NH_4OH + CO_2 = NH_4HCO_3$$

or

$$2NH_4OH + CO_2 = (NH_4)_2CO_3 + H_2O$$
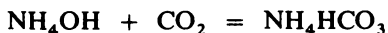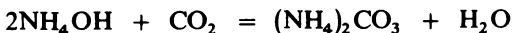
and condensate becomes alkaline (pH $\geqslant$ 8.3). Getting into a boiler

unit, ammonia carbonate decomposes

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + \overset{\bullet}{H_2O}$$

and the processes considered repeat. Since in the deaerator and turbine condenser a fraction of ammonia (8 to 10%) is removed from the system, the chemical must be introduced into the feedwater continuously. Ammonia is introduced in an aqueous solution, NH_4OH, or as a solution of some salt of ammonium, NH_4Cl, $(NH_4)_2SO_4$. In the latter case it must be borne in mind that water-dissolved ammonium salts are potentially acid and can only be used if boiler water is sufficiently alkaline.

To prevent the appearance of acid water in boiler units when feedwater contains ammonium salts of strong acids (for instance, when feedwater is treated in sodium-ammonium-cation-exchange plants, see Sec. 10.1), care must be taken that the hydrate alkalinity A_h^{fw} satisfies the condition

$$A_h^{fw} - C_{[NH_3]} \geqslant 0.5 \text{ mg-equiv/kg} \tag{5.2b}$$

where $C_{[NH_3]}$ = concentration of ammonia in feedwater.

When this defference exceeds 0.5, NaOH must be introduced into feedwater to make valid inequality (5.2b).

5.4. Corrosion of Boiler Units

5.4.1. Oxygen Corrosion

Oxygen corrosion most often occurs in steel water economizers of boiler units. If feedwater is poorly deaerated, steel economizers can fail in 2 or 3 years after being put into service.

Oxygen corrosion of steel economizers results in the formation of flaws in tubes, through which water can rush at a great velocity. When directed toward the surface of an adjacent tube, the jets of water erode the tube so that through holes can form in it. Inasmuch as economizer tubes are rather closely arranged, the flaw formed due to corrosion can be the cause of damage to a large number of tubes if the boiler is long kept in service after occurrence of the flaw. Iron economizers do not suffer oxygen corrosion.

Oxygen corrosion is most commonly encountered in the inlet sections of economizers. However, if oxygen concentration in

feedwater is sufficiently high, oxygen penetrates into the boiler unit too. In the boiler unit, corrosion mainly occurs in drums and downcomer tubes. Riser tubes (steam generating tubes) suffer from oxygen corrosion to a considerably lesser extent, which is due to the deaerating action of the steam bubbles forming in these tubes. Oxygen corrosion shows up mainly as pitted spots on a metal that eventually result in the formation of flaws.

An increase in pressure intensifies oxygen corrosion. That is why even the "breakthrough" of small amounts of oxygen in deaerators is hazardous to boiler units operated at a pressure of 10.0 MPa and higher. The composition of the water which comes into contact with a metal is of paramount importance. Even a small amount of alkali intensifies local corrosion, while chlorides cause corrosion over the entire surface of metal.

5.4.2. Outage Corrosion

Idling boiler units are subject to electrochemical corrosion, which is known as outage (out-of-service) corrosion. For maintenance reasons boiler units have to be often taken out of service and left shutdown for a long time. When a boiler is laid up for banking purposes, the boiler pressure drops gradually and then a rarefaction (vacuum) develops in the drum that causes air infiltration and enrichment of boiler water with oxygen. This leads to the initiation of oxygen corrosion. Even when water is completely removed from the boiler unit, its internal surfaces remain wet. Variations in the air temperature and humidity cause condensation of the water vapour from the air contained in the boiler unit. The film of moisture that covers metal surfaces becomes enriched with oxygen as air forces its way into the boiler and thus contributes to the development of electrochemical corrosion. If the internal surfaces of the boiler unit are covered with deposits capable of dissolving in the moisture film, the intensity of corrosion increases considerably. Phenomena of this kind can be observed, for instance, in superheaters that often suffer from outage corrosion. That is why when laying up a boiler for a long outage time, all deposits present in it must be removed by washing.

Outage corrosion may cause much damage to boiler units unless special protective measures are taken. Moreover, the corrosion centres that have originated in the period of idling continue to act after the units are put into operation.

There are many methods of preventing corrosion when boilers are taken out of service, among which one can list the following:

1. The method of placing boiler units in dry storage.

The shutdown boiler unit is allowed to cool down, all mains and pipelines are cut off by means of stoppers, water is drained, then the deposits are removed and the surfaces dried. While drying goes on, all air vents are kept open. After drying is terminated, trays filled with water absorbers or packed water absorbers ($CaCl_2$, CaO, silica gel) are placed into the drums in amounts of about 1.5 to 2.0 kg of the absorbing agent per cubic metre of boiler-unit volume. All manholes and stop fittings are tightly closed. In the event of long-time outage, the water absorber is checked periodically for condition and replaced if necessary.

2. Wet storage. Filling the boiler unit with feedwater and holding it under excess pressure. The shutdown boiler unit (drum type) is allowed to cool down and then is blown from the bottommost points to ensure removal of sludge; the boiler unit is cut off of all water- and steam lines, filled with deaerated water and left to stand under a deaerator pressure. When put into wet storage after repairs, the boiler unit is filled with deaerated water to the normal level, lighted up and air-vented at 0.2 MPa for 2 or 3 h to remove completely oxygen from the water. The boiler unit is then kept in storage under an excess pressure.

3. Coating the internal surfaces of a boiler unit with a film of a 10 per cent sodium nitrite solution. This method is applicable to low-capacity boiler units of low and intermediate pressures. The film can be applied in two ways: the boiler unit is filled with the $NaNO_2$ solution, which is kept there for 20-30 min and then drained off into a tank for repeated usage; by the second method, the internal surfaces are wetted with the $NaNO_2$ solution. After drying, the metal surface is found to be coated with a thin film of the concentrated solution that passivates the metal. This film must be washed off and the solution drained before putting the boiler unit into operation.

4. Filling the boiler unit with a hydrazine solution. After its shutdown, the boiler unit is blown through the bottommost points at a low pressure to remove sludge. Then, at a pressure of 0.3 or 0.4 MPa, the boiler unit is filled with deaerated water to the normal level and, using a metering pump, a 3 to 5 per cent solution of hydrazine and sodium hydrate is introduced into water to a concentration of 200 to 250 mg N_2H_4 per kg boiler water. The

water in the steam generator is boiled for 1 or 2 h to ensure proper mixing of the reagent and water. Then the boiler unit can be filled completely with deaerated water and connected to a deaerator. In this method, it is not necessary to maintain an excess pressure. A new portion of hydrazine must be introduced when its concentration in the solution drops to 100 mg/kg. When put into storage after repair, the boiler unit is filled with water to the normal level, the water is boiled for 1 or 2 h to remove O_2, and then hydrazine is introduced. The following stages are the same as indicated above.

5. Connecting the boiler unit to a source of saturated steam at a pressure of 0.2 or 0.3 MPa. The excess pressure is created by the saturated steam taken, for instance, from a blowdown flash tank, steam extraction line of suitable pressure, or from some other appropriate source. First, the shutdown boiler unit is blown through all bottommost points to remove sludge, then pressure is reduced to 0.2 or 0.3 MPa and the boiler unit is connected to the steam source available.

6. Treating the internal surfaces of a boiler unit with complexing agents. After its cooling and disconnection from all mains, the boiler unit is drained and filled with a solution of trylon B with a concentration of 300 to 800 mg/kg. The solution is prepared in tanks using nondeoxygenated water (but free of NH_3 and N_2H_4) because oxygen ensures a more efficient treatment. The solution is delivered to the boiler unit and superheater to fill them up completely, and then the boiler unit is lighted up slowly. The steam formed is discharged through the blowdown line of the superheater, and excess water through the drainage pipe of the economizer. During 4 to 6 h (first stage) the pressure is maintained at a level corresponding to a saturation temperature of 423 K. Then the pressure is raised gradually (for 3 to 5 h) to the operating level, which is maintained for 1 or 2 h (second stage). During this kind of treatment it is desirable to add as little water as possible. After treatment, the boiler unit can be put into operation without replacing water.

With this method of treatment, a highly corrosion-resistant film forms on the water-side surface of carbon steel. Boiler units treated by this method can be taken out of service for repairs and left open, not fearing corrosion of water-side surfaces. Surfaces treated with trylon B are resistant to corrosion for 1.5 to 2.0 years. Scale deposits, if any, should be removed before treatment. This method

is not suitable for boiler units operated at pressures below 0.4 MPa.

7. Preparing for storage by using nitrogen. By this method, the boiler unit, turbine, and heat exchangers are filled with nitrogen containing no more than 0.5 per cent O_2, then a certain pressure is built up and maintained during the entire idling period. Methods of keeping in storage supercritical-pressure once-through boiler units are chosen depending on the reasons and duration of idling. But all these methods use either nitrogen or solutions of hydrazine, ammonia or trylon B.

5.4.3. Intercrystalline Corrosion

Intercrystalline (intergranular) corrosion occurs in riveted and expended joints of boiler units that are exposed to boiler water. First the metal develops fine cracks invisible to the eye, which then grow with time and become quite discernible. The cracks run between grains (crystallites) of the metal, for which reason this kind of corrosion is known as crystalline. The metal fractures without showing any signs of deformation (strain) that usually accompanies its destruction in other cases. Disintegration caused by intercrystalline corrosion is therefore called brittle, *strainless*. This type of destruction is not observed in riveted or expanded joints exposed to steam.

Experience shows that intercrystalline corrosion appears only when the following three factors are present and act simultaneously: (1) high tensile stresses in metal, close to the yield point; (2) leakinesses in riveted or expanded joints; (3) aggressive properties of boiler water. In the absence of any one of the three factors, fractures do not occur at all. This condition is given due consideration in organizing control of intercrystalline corrosion.

Of the three factors mentioned, the first should be considered most important. An analysis of the reasons for the appearance of intercrystalline corrosion in boiler units shows that the primary cause is largely thermal strain in boiler elements accompanied by high stresses in the metal. It originates due to nonuniform heating or cooling of components, rapid reduction in boiler load, fast cooling of a boiler unit, shut down for technical reasons, etc. Rapid and nonuniform cooling or heating of drums causes warpage and disturbs the air-tightness of riveted and expended joints. As a result, circular cracks appear in tubes, usually at spots where an expansion tool was used.

When starting up or shutting down a boiler unit, its component elements (waterwalls, water drum) deform or change their position. These displacements should be controlled when carrying out such operations so as to make sure that a given element is free to expand. Clamping of a movable (expanding) element causes dangerous stresses in the metal.

Intercrystalline cracks can also develop under local cooling of small sections of a boiler drum. Such undesirable cooling is likely to occur at spots where the feedwater lines, intermittent-blowdown pipes, phosphate solution feed pipe, and water-gauge pipes are connected to the drum. The drum metal cools in all these expansion joints if the temperature of the liquid flowing in the tube is lower than the saturation temperature. Local cooling of drums is always responsible for the appearance of high stresses in metal. That is why relatively cold flows of liquid are delivered into a boiler drum by using heat-insulating jackets (Fig. 5.4) to isolate the flows from drum *1*.
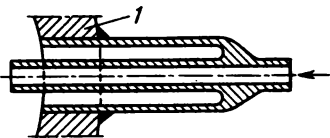
Fig. 5.4. Heat-insulating jacket

Fracturing is the most hazardous process as it often leads to major accidents, yet its origination and development in the initial period is not amenable to control. However, intercrystalline corrosion is accompanied by phenomena that may be indicative of its presence. Such indications are the formation of salt outgrowths at the edges of seams or heads of rivets, recoil or rattling of rivet heads on tapping them with a hammer when a boiler unit is laid up for repair, steaming and leakage through riveted and expansion joints. When these defects or one of them is detected, drums should be thoroughly checked for the presence of intercrystalline cracks.

The aggressivity of boiler water is specified by the composition of the salts contained (dissolved) in it. Of particular concern is the content of sodium hydrate that reacts with metals when its concentrations are high (5 to 10 per cent). It is exactly such concentrations that are observed in loose riveted and expansion joints where evaporation of boiler water takes place. Evidently, the

presence of leakinesses in joints may be the cause of fracturing under certain conditions. In addition, an important indication of the aggressivity of boiler water is its relative alkalinity A_r, %, determined by the expression

$$A_r = \frac{40 \, (A_{bw} - 0.02 C_{PO_4^{3-}}) \, 100}{S_{bw}} \, 100 \tag{5.3}$$

where $C_{PO_4^{3-}}$ is the concentration of phosphate ions in boiler water, measured in mg/l. It is believed that for prevention of fracturing, the relative alkalinity of boiler water should not exceed 20 per cent. Relative alkalinity depends on the composition of initial water and the method of its treatment, provided that chemically treated water is used as makeup for boiler units.

The methods used to guard against the formation of fractures include measures undertaken to eliminate one of the above enumerated factors leading to their appearance. They are aimed above all at excluding nonuniform heating or cooling of drums, checking for the expansion of boiler pipelines, observing starting-up and shutdown instructions, using heat-insulating jackets, etc. Thus, the purpose of these measures is to eliminate excessive stresses and leakinesses in joints. Often, riveted drums are replaced by welded ones, and expansion joints by welded joints.

Two methods of controlling aggressivity of boiler water are applied. The first, known as the nitrate treatment method, makes use of dissolved sodium nitrate. The concentration of sodium nitrate in boiler water (mg/l) must meet the following condition

$$C_{NaNO_2}/40 A_{bw} \geqslant 0.35\text{-}0.4 \tag{5.4}$$

Nitrates passivate metal and thus protect it against corrosion. The method of nitrate treatment, though rather effective in practice, is applicable only to boiler units operated at pressures not higher than 7.0 MPa, because at higher pressures sodium nitrate decomposes and the treatment becomes meaningless.

For boiler units operated at pressures higher than 7.0 MPa, the second method is applied chiefly to remove the aggressive free sodium hydrate from boiler water. It is known as the method of purely phosphate alkalinity. Its essence consists in that boiler water is treated so that its alkalinity is governed only by trisodium phosphate (see Subsec. 3.4.2).

5.4.4. Vapour-Water Corrosion

Vapour-water corrosion causes destruction of a metal due to its chemical interaction with water vapour

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$
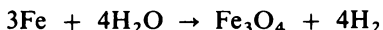
Carbon steels can undergo destruction when the temperature of tube walls rises to 673 K and higher; for alloyed steels it must be above 803-858 K. The corrosion products here are gaseous hydrogen and magnetite. Both uniform and local vapour-water corrosion occur in metals. In the first case, the surface of metal becomes covered with a layer of corrosion products, sometimes of a silvery colour. Local corrosion shows itself as pits, groovings and cracks.

Vapour (steam) corrosion mostly originates when the wall of a tube heats to a critical temperature at which the reaction of metal oxidation under the action of water proceeds at a greater rate. Of the number of factors that contribute to corrosion of metals by vapour, one should note the following: disturbed circulation in steam-generating tubes, high rates of heat flow (equal to or over 230×10^3 W/m^2), appearance of film-type boiling which leads to metal overheating.

In accordance with the foregoing, vapour-water corrosion occurs in superheaters and in steam-generating (waterwall) tubes of boiler units, whose temperature reaches critical values for some reason or other.

Vapour-water corrosion is controlled and prevented by eliminating the causes responsible for tube overheating. It will be noted that this kind of corrosion cannot be prevented by changing or improving water control of boiler units, since its causes lie in the hydrodynamic processes specific to furnaces and boiler units and also in operating conditions.

5.4.5. Hide-Out Corrosion

This kind of corrosion occurs under a layer of sludge settling on the water-side surfaces of boiler-unit tubes. The chemical composition of sludge depends on the composition of the impurities getting into a boiler unit with feedwater. In this way hide-out corrosion may appear when a boiler unit is fed with insufficiently treated water containing suspended substances that form a solid

phase (sediment). This can take place in boiler houses fitted with low-capacity and low-pressure drum•type boiler units (<4.0 MPa) firing high-energy fuel (gas, mazute).

With hide-out corrosion, a metal suffers local (honeycomb-kind) damage usually on the side of a tube facing the furnace. The pits or cavities that form on the metal take the shape of a shell up to 20 mm in diameter and more. They are filled with iron oxides that bulge over the pits (Fe_3O_4 at the bottom and Fe_2O_3 at the top). Damage of this kind usually occurs underneath a layer of iron-oxide deposits. Phosphate sludge does not cause such damage. The main chemical process responsible for hide-out corrosion is the reaction between iron and hard depolarizer, Fe_2O_3:

$$Fe + 4Fe_2O_3 \rightarrow 3Fe_3O_4$$
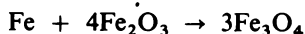
So, iron-oxide depositions, which mainly consist of Fe_2O_3, provoke not only scale formation but also corrosion, since this composition acts as an oxygen supplier. Hide-out corrosion often combines with vapour-water corrosion since the metal underneath a layer of sludge can heat to the critical temperature.

The main method of preventing hide-out corrosion consists in precluding penetration into a boiler unit of large amounts of iron oxide, Fe_2O_3, and copper oxides, CuO, Cu_2O. In this connection, while elaborating the design of a water-treatment plant for a boiler house, it is important to consider a flow diagram involving the supply of steam to and its usage by consumers so as to ensure a minimum iron concentration ($\leqslant 100\ \mu g/kg$) in industrial condensate delivered to the boiler house.

5.5. Water Control Methods for Supercritical-Pressure Boiler-Turbine Units

Water-condensate circuits of supercritical-pressure boiler-turbine units are subject to more or less intensive corrosion. The products of corrosion of steel and copper alloys contaminate feedwater. To keep water-condensate circuits from corrosion, they must operate under conditions that enable slowing down corrosion processes. Various methods exist for the purpose, some of which will be considered below.

5.5.1. Alkaline (Correction) Method

This method of water control is now most widespread at Soviet district power plants and heat and power stations. Feedwater for supercritical-pressure boiler units is found to be least aggressive if its pH value is kept equal to 9, since this favours the formation of a sufficiently strong protective film on the surface of steel, which heavily reduces the intensity of corrosion. The pH value is kept equal to 9.0-9.2 by introducing ammonia into the water-condensate circuit, seeing that the concentration of this chemical does not exceed 800 µg/kg. In water, ammonia dissociates following the reaction

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^- \tag{5.5}$$
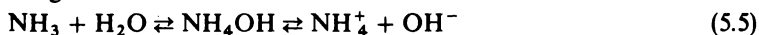
Ions, OH^-, so formed, ensure the prescribed pH value. In addition to NH_3, hydrazine, N_2H_4, is also added in preset quantities into feedwater. This strong reducing agent binds the water-dissolved oxygen and reduces its oxidizing potential, thereby slowing down corrosion processes.

The spot where ammonia and hydrazine are introduced into the flow circuit of a boiler-turbine unit is of much importance. It has been found that it is most expedient to introduce hydrazine downstream of the demineralizing plant, and ammonia downstream of either the low-pressure regenerative feedwater heater or the deaerator. After the demineralizing plant, the pH value of condensate becomes less than 9. However, introduction of NH_3 after the demineralizing plant intensifies corrosion of the brass heating surfaces of low-pressure regenerative feedwater heaters and increases the concentration of copper in condensate upstream of the deaerator over the prescribed values (5 µg/kg), which should not be tolerated.

With increasing water temperature, which rises from 303-308 K to 528 K in the circuit of a boiler-turbine unit, the equilibrium of reaction (5.5) shifts from the right to the left, i.e. the dissociation constant of NH_4OH diminishes. This leads to a decrease of pH in the steam-condensate circuit of the boiler-turbine unit. For this reason, to maintain the value of pH equal to 9, the concentration of ammonia must vary in different sections of the circuit. Fig. 5.5 gives the plot of the required concentrations of NH_3 versus temperature. At a temperature of 453 K (pH = 6.44 in the first high-pressure regenerative feedwater heater, as viewed in the direction

of water flow), the concentration of NH_3 required to keep pH equal to 9 is 600 µg/kg; at 523 K (pH = 6.22* at the boiler unit inlet) a concentration of about 1400 µg/kg̊ must already be ensured. In the condenser (303 to 308 K), such a concentration will increase the pH value to 9.5 or 9.6, which is inadmissible due to the danger of corrosion of brass tubes. The problem becomes more involved when CO_2 of variable concentrations penetrates into the circuit.
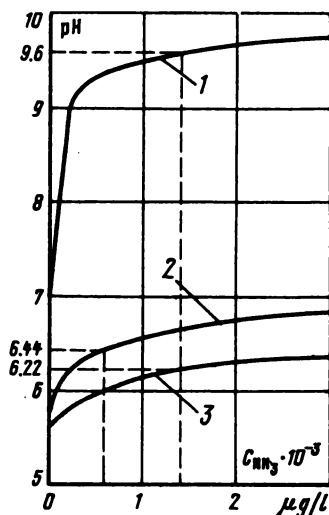

Fig. 5.5. pH value versus ammonia concentration and temperature

1 — 298 K; *2* — 453 K; *3* — 523 K

The foregoing shows how difficult it is to maintain anticorrosive conditions in all sections of the circuit when ammonia is used as an alkaline compound. There exist, however, substances, called alkaline amines (morpholine, piperidine, cyclohexylamine), that may be used successfully to replace ammonia. These chemicals, taken in considerably lesser concentrations than NH_3, noticeably simplify the task of maintaining the required pH value in different sections of the circuit. What hinder a wider usage of these substances in practice so far are their shortage and high cost.

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* The pH value diminishes with increasing temperature (see Sec. 1.4 and Fig. 1.6).

5.5.2. Water Control by Complexing Agents

This corrosion-preventing method uses a complexing agent (EDTA) in addition to hydrazine and ammonia for treatment of water in water-condensate circuits. The treatment ensures the formation of a dense magnetite film that strongly adheres to the surface of metal and protects it against corrosion. This method of feedwater treatment was considered in greater detail in Sec. 3.4.

5.5.3. Neutral (Correctionless) Method

At the present time this method of water control is being tried out and elaborated in industry. The method requires no chemical reagents for introduction into the water-condensate circuit of a boiler turbine unit and relies entirely on the use of gaseous oxygen or hydrogen peroxide. At high pressures and temperatures and with sufficiently clean water used, oxygen is capable of creating on the steel a protective film that inhibits corrosion. This method of water control demands that a number of requirements and conditions should be strictly observed. Condensate and feedwater must be deeply deionized (be rid of electrolyte ions). The conductivity of such water should not exceed $0.15 \, \mu S/cm$ at 298 K, pH should lie within 7.0 to 7.5, and the concentration of O_2 from 20 to $200 \, \mu g/kg$ at about 473 K and 10 to $40 \, \mu g/kg$ at a temperature above 473 K.

Thus, two basic parameters determine the effectiveness of this method, namely, the conductivity of feedwater (the extent to which ionic impurities are removed from it) and oxygen concentration. The first parameter is more rigidly standardized than the second.

The replacement of the alkaline method of water control by the neutral method offers a number of advantages such as a saving in reagents (NH_3, N_2H_4, H_2SO_4, $NaOH$), longer operational period between regenerations for ion-exchange softeners of the demineralizing plant, and simplified chemical control. However, with the neutral method used, the low-pressure regenerative feedwater heaters must have steel tubes.

The first results of tests carried out on supercritical-pressure boiler-turbine units have shown that with this method of water control the concentration of iron in the water-condensate circuit decreases. Besides, less iron oxides settle on the internal heating surfaces and the wall temperature of steam-generating tubes grows slower.

5.5.4. High-Alkalinity (Correction) Method

This method differs from the alkaline one in that a high pH value, equal to 9.4 or 9.5, is maintained in the water-condensate circuit of a boiler-turbine unit at the expense of a higher ammonia concentration in water. Experience shows that this method is highly effective; it reliably protects pipelines and equipment against corrosion. This method, however, calls for the replacement of the brass tubes of low-pressure regenerative feedwater heaters by steel tubes (made from perlitic grades) and use of an ammonium-cation exchange material in the intermediate-pressure softeners of the demineralizing plant instead of the H-cation exchange material applied in conventional alkaline methods (pH = 8.9 to 9.1). It should be borne in mind that at pH > 9.1 corrosion of copper tubes proceeds at higher rates and the concentration of copper in feedwater increases materially; subsequently, this copper settles on turbine blades and lowers turbine efficiency.

Review Questions

1. What is the essence of the method of dry storage of idling boiler units?

2. What factors are responsible for electrochemical corrosion of metal?

3. Is it possible to detect intercrystalline corrosion of metal in boiler units in an early stage and what are its signs?

4. What conditions are responsible for the appearance of intercrystalline corrosion?

5. Explain the mechanism of intercrystalline corrosion. What distinguishes this kind of corrosion from chemical corrosion?

6. Calculate the amount of oxygen involved in the oxidation of 1 g of iron to Fe_2O_3.

Chapter 6

Deaeration and Deoxygenation of Water

6.1. Thermal Deaeration of Water

6.1.1. General

Deaeration (degasification) is the process of removing from water dissolved corrosive gases — oxygen and carbon dioxide. The removal of only oxygen from water is called *deoxygenation*. Water is deaerated by a thermal method, and deoxygenated by chemical techniques.

Thermal deaeration of water is based on the fact that the solubility of gases in water decreases as their partial pressures drop off in the space above the water, for which purpose water is heated to the boiling point at the given pressure. The pressure exerted on the water being deaerated has practically no effect on deaeration. For this reason, deaeration can be realized both at a pressure higher and lower than the atmospheric, i.e. in a vacuum.

Water is deaerated in apparatus called deaerators. According to pressures under which they operate, deaerators are classified as vacuum, $p < 1.16 \times 10^5$ Pa, atmospheric, $p = (1.2$ to $1.7) \times 10^5$ Pa, and higher-pressure deaerators, $p = (1.7$ to $7.0) \times 10^5$ Pa. Atmospheric-type deaerators can in turn be subdivided into direct-contact (mixing) deaerators and overheated-water deaerators. In addition, film-type, atomizing, and tray-type deaerators are distinguished, in accordance with the way in which steam and water are distributed in them.

6.1.2. Direct-Contact Deaerators

An atmospheric direct-contact deaerator is depicted in Fig. 6.1. It consists of deaerator proper *1* and storage tank *2* for deaerated water. The storage tank is fitted with water gauge glasses *3*, pressure gauge *4*, hydraulic (water) seal *5* to prevent production of a high pressure or vacuum in the deaerator, and a thermometer on
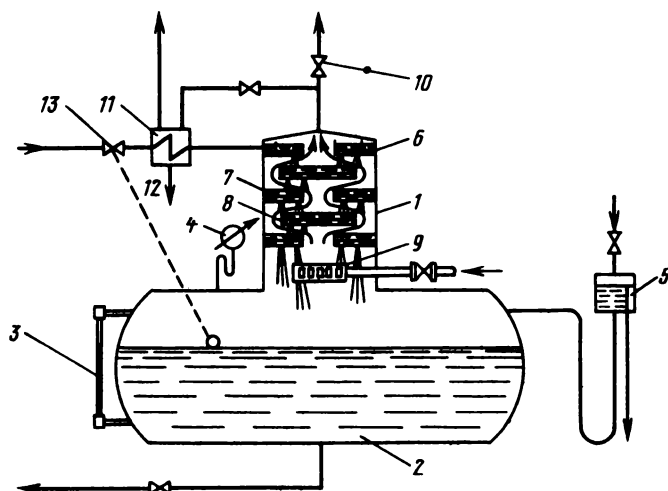
Fig. 6.1. Direct-contact (mixing) atmospheric-pressure deaerator

the outlet connection through which deaerated water is drawn by the feed pumps.

Water enters the deaerator at the top through distributing device *6*, below which trays *7* and *8* are arranged. In the flat bottoms of the trays there are perforations 5 to 7 mm in diameter, through which water flows in streams and falls from the first tray on to the second, from the second on to the third, etc. In a properly operating deaerator, the space between the trays is filled with streams forming a shower screen. Heating steam is delivered into the lower section of the deaerator through steam distributor *9*. Steam goes upward gradually, crossing the streams of water that fall from the trays. The gases evolved from the water together with the noncondensing vapour are vented from the deaerator into the atmosphere through valve *10*, or pass into vent condenser *11* where the steam condenses as it gives up heat to the water flowing to the deaerator, and the condensate is directed into drain tank *12*. The water, heated to the boiling point and freed from the gases, gets into the storage tank, whence it is drawn by the feed pumps. The storage tank is an important component of the deaerating plant because here the water gives off the remaining gas. Besides,

desorption takes place in the storage tank. Deaerators are usually fitted with automatic steam- and water-flow controllers *13*.

Individual streams of water, not fully degasified in the deaerator, may get into the storage tank due to a number of reasons. To remove oxygen and carbon dioxide that get into the storage tank and to raise the degree of sodium bicarbonate decomposition, in modern deaerators steam is blown through the water. This process, known as *steam-jet deaeration*, is carried out in the storage tank fitted with suitable arrangements. Water is stirred intensively and maintained in a state of boiling, which contributes to a more complete removal of dissolved gases and a greater degree of bicarbonate decomposition. The demerit of steam-jet deaeration is that it necessitates the use of steam of increased pressure.

The design of deaerators and their operating conditions must satisfy a number of requirements, of which emphasis must be placed on the following:

1. The temperature of deaerated water must be equal to the saturation temperature corresponding to the pressure in the deaerator. For atmospheric-type deaerators, the temperature of deaerated water is taken as 373.3 K at $p = 1.2 \times 10^5$ Pa. So, in operating a deaerating plant, it is necessary to take into account not only the temperature of deaerated water, but also the absolute pressure in the deaerator. It should be borne in mind that pressure gauges indicate excess pressure p_{pg}, and the boiling point of water in the deaerator depends on absolute pressure equal to the sum of pressures, p_{pg} and p_b, indicated respectively by a pressure gauge and a barometer.

2. The amount of heating steam delivered to a deaerator must correspond to the quantity of heat required to ensure continuous boiling of the water undergoing deaeration. Insufficient steam supply causes a drop in deaerator pressure and a decrease in the effect of water deaeration. This requirement is satisfied to best advantage through the use of automatic control of deaerating plants.

3. Deaerated water must be broken into sufficiently fine droplets so as to provide a maximum surface of contact between the water and heating steam. This is essential not only for ensuring better heat transfer between the heating steam and water, but also for speeding up the evolution of gases dissolved in water. In modern deaerating plants, the free water surface is increased in a number of

ways. Tray-type deaerators have found the widest application, in which water is separated into individual streams by means ~of perforated trays. Use is also made of film-type deaerators, in which water is separated into thin films. One of the methods of separating water into films is to fit a deaerator with a packing built up of small-size elements such as rings, differently bent plates, and small-size cylinders. The water passing into the packing is separated into films flowing down over the surface of the elements.

4. Sufficient venting of the deaerator must be ensured so as to evacuate from it all noncondensing gases and thereby provide for a minimum partial pressure of these gases in the upper section of the deaerator. This is accomplished by continuously removing from the deaerator a gas-vapour mixture called *vent*. The amount, or volume, of vent has a material effect on degasification, as can be seen from Fig. 6.2. To effect steady deaeration of water, the amount of vent must be no less than 1.5 to 2.0 kg per ton of deaerated water. When the water undergoing deaeration contains free and bound carbon dioxide, the rate of venting increases to 2 or 3 kg/t.

5. When several deaerators are operated in parallel, the same pressure must be maintained in them so as to preclude water flow
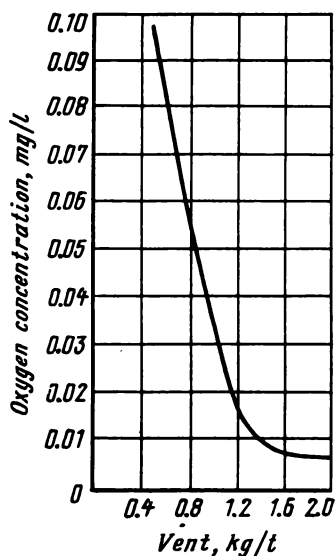
Fig. 6.2. Oxygen concentration in deaerated water as a function of the amount of vent

from one storage tank into another. An equal pressure is ensured by connecting the steam spaces of the deaerators with an equalizing line or by delivering steam to the deaerators from one steam main of sufficiently large diameter, in which a constant pressure is maintained.

The performance of a deaerator greatly depends on the rate of water flow through it and temperature of the water undergoing deaeration. If the temperature of deaerated water is low, the cross-sectional area of perforations for steam flow is small and the rate of water flow is large, hydraulic impacts are likely to occur in the deaerator, in which case the rate of water flow through the deaerator must be decreased.

In an atmospheric-type deaerator operating without steam-jet deaeration, efficient removal of CO_2 from the water and partial decomposition of $NaHCO_3$ can be achieved if the concentration of CO_2 in the heating steam does not exceed 3 to 5 mg/l, the time during which water remains in the storage tank is not more than 15 min, and the bicarbonate alkalinity of deaerated water is not less than 0.3 mg-equiv/l. Otherwise, steam-jet deaeration is required. An increased content of oxygen and carbon dioxide in the water can be attributed to many causes, of which the following are most essential: an insufficient amount of vent; an inadmissibly high rate of water flow through the deaerator at the given water temperature; supply of oxygen-containing condensate directly to the storage tank along with the delivery of such condensate to the deaerator; periodical pumping of industrial condensate or regenerative feed-water-heater condensate into the deaerator; delivery of relatively "cold" flows with an increased O_2 content into the deaerator on to the second or third tray; delivery of overheated condensate on to the second tray; faulty deaerator internals; delivery of the vapour (vent) from several deaerators into one manifold; disturbed operating conditions of the deaerator (frequent drops in pressure).

6.1.3. Vacuum Deaeration

At modern electric power stations, water deaeration at $t > 373$ K is the main method of removing corrosive gases from water. Some consumers, however, require water at $t < 373$ K, such as low-capacity low-pressure boiler units, hot-water supply systems and others. In this case, the method of vacuum degasification may prove most suitable. The essence of this method consists in that

a vacuum (rarefaction) is created and maintained in a deaerator. The amount of vacuum depends on the temperature of the water degasified—the lower the temperature, the higher must be the vacuum, which is rather difficult to maintain at a given level. Nevertheless, vacuum deaerators have found wide application. Their design is in general similar to that considered above (see Sec. 6.1).

At electric power stations, turbine condensers serve in the capacity of high-throughput vacuum deaerators, in which a 95 to 97 per cent vacuum is maintained. That is why the makeup water for turbine-boiler units operated at electric power stations is treated in turbine condensers.

6.2. Chemical Deoxygenation of Water

6.2.1. Sulphite Treatment

The chemical method of water deoxygenation by means of reagents is based on binding water-dissolved oxygen with the aid of substances capable of intensive chemical interaction with oxygen dissolved in the aqueous solution. Examples of such substances that find industrial application are sodium sulphite, Na_2SO_3, and hydrazine, N_2H_4.

Water treatment with sodium sulphite is based on the oxidization of the sulphite by the water-dissolved oxygen following the reaction

$$2Na_2SO_3 + O_2 = 2Na_2SO_4 \tag{6.1}$$

In practicing this method, it is of importance that the reaction should be completed over the time interval during which water flows from the spot where the chemical is introduced to the equipment being protected, in particular to a boiler-unit economizer. For this purpose the water temperature should be maintained at 353 K and an excess amount of sulphite at 2 mg/l. Sodium sulphite is added into water as a 3 to 6 per cent solution by means of a variety of metering devices in a quantity calculated by the formula

$$C_{Na_2SO_3} = 8C_{O_2} + 2 \tag{6.2}$$

where $C_{Na_2SO_3}$ = concentration of sodium sulphite solution, mg/kg
C_{O_2} = concentration of water-dissolved oxygen, mg/kg

When determining the consumption of commercial sulphite, crystallization water, $Na_2SO_3 \cdot 7H_2O$, must be taken into account.

The sulphite solution absorbs atmospheric oxygen and turns into inert sulphate. That is why when preparing and keeping in storage dissolved Na_2SO_3, care is taken to isolate it from the atmosphere. An example of the layout of equipment used for preparation of sulphite solutions is illustrated in Fig. 6.3. Crystalline sodium sulphite
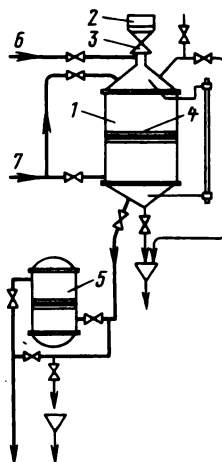

Fig. 6.3. Layout for preparing sulphite solutions

is charged into dissolver *1* through funnel *2* and gate valve *3*, in which the chemical is arrested on grid *4*. The dissolver is purged with steam *7* to remove air before filling the apparatus with water *6*. Dissolution of the chemical is speeded up by delivering steam into the lower section of the dissolver to effect heating and stirring of the solution. The finished solution is passed through cloth bag filter *5* and then delivered to metering devices.

The merits of sulphite treatment of water are as follows: it is simple to realize, available to many small consumers, and requires no large-size and expensive equipment. The demerit of this method of water treatment is that it increases the content of total solids in feedwater by about 12 mg per mg of dissolved oxygen. Since the concentration of dissolved oxygen in natural waters reaches 8 to 10 mg/l, an increase in the content of total solids can run as high as 100 to 120 mg/l. Therefore, at some industrial power plants sulphite treatment of feedwater is used for binding the traces of oxygen in

thermally deaerated water, i.e. for additional deoxygenation of water. In these conditions ($t > 373$ K), reaction (6.1) proceeds fast at a minimum excess of sulphite, whose quantity does not commonly exceed 2 mg/l.

6.2.2. Hydrazine Treatment of Water

Hydrazine, N_2H_4, being a strong reducing agent, has found wide application in preventing corrosion of up-to-date heat-power equipment that operates under high and supercritical steam conditions. It is available in hydrazine hydrate, $N_2H_4 \cdot H_2O$, and hydrazine sulphate, $N_2H_4 \cdot H_2SO_4$. The first reagent, a colourless liquid, readily absorbs from air CO_2, O_2, and moisture and has weak alkaline properties; the second is a solid substance, poorly dissolves in cold water and possesses acid properties.

Hydrazine binds dissolved oxygen following the reaction

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{6.3}$$

which proceeds at an appreciable rate only at $t \geqslant 373$ K. An increased pH value also has an added effect on the reaction rate.

At pH = 9 to 9.5, $t \approx 376$ to 378 K and with a hydrazine excess of about 20 µg/kg, it takes 2 or 3 seconds to bind O_2. At pH < 7, hydrazine fails to prevent corrosion and even intensifies it to some extent. Hydrazine hydrate does not increase the content of total solids in feedwater and yields no harmful volatile decomposition products, which makes it a suitable reagent for use in once-through boiler units. Hydrazine sulphate can only be used for treating feedwater of drum-type boiler units.

This kind of treatment consists in continuous introduction of metered quantities of hydrazine into the water undergoing deoxygenation. The treatment results not only in binding oxygen by formula (6.3), but also in reducing all the metal oxides present in water:

$$4Fe(OH)_3 + N_2H_4 \rightarrow 4Fe(OH)_2 + 4H_2O + N_2$$

$$6Fe_2O_3 + N_2H_4 \rightarrow N_2 + 2H_2O + 4Fe_3O_4 \quad \left.\right\} \tag{6.3a}$$

$$2CuO + N_2H_4 \rightarrow 2Cu + 2H_2O + N_2$$
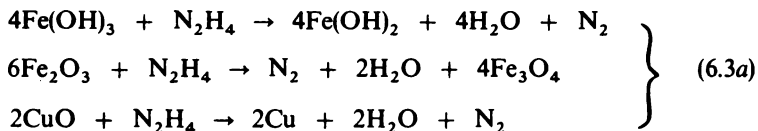
The presence of iron- and copper oxides in water, in addition to oxygen, complicates the way in which hydrazine interacts with these substances. Reactions (6.3a) can proceed at a higher rate in certain

conditions than reaction (6.3), and consequently the latter reaction becomes of secondary importance.

Hydrazine consumption is calculated by the formula

$$q_h = 3C_1 + 0.3C_2 + 0.15C_3 \qquad (6.4)$$

where C_1, C_2 and C_3 denote the concentration of O_2, Fe_2O_3, CuO and Cu_2O in feedwater, respectively.

Hydrazine can be used to control nitrite corrosion in high-pressure boiler units. It is used for putting into storage boiler units and other heat-handling apparatus, and also for hydrazine-acid cleaning of heat-power equipment. Hydrazine is introduced into a boiler unit as a solution of definite concentration by metering pumps. Hydrazine and its solutions are noxious. They must be handled with great care according to prescribed safety rules, using protective devices (goggles, breathing masks, gloves).

Under certain conditions, excess hydrazine undergoes decomposition accompanied by the formation of ammonia

$$3N_2H_4 \rightarrow 4NH_3 + N_2$$
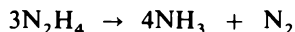
The rate of this reaction depends on the ambient temperature, the pH value of water, etc. When hydrazine is used in the heat cycle, care must be taken that the accepted or admissible excessive amounts of hydrazine should decompose completely in the circuit of the heat-power equipment and not pass to steam and water consumers.

Review Questions

1. What mechanism is involved in the removal of dissolved oxygen in a deaerator? What conditions should be observed in the process?

2. Basing upon the oxygen absorption coefficient (see Fig. 1.5), explain how pressure affects the solubility of oxygen.

3. Name the methods of water deoxygenation and the field of application of each.

4. Basing upon the decomposition reaction for NO_2^- (see Sec. 5.1), explain how water alkalinity affects the process of decomposition. Does it speed up or decelerate the process?

5. Waters containing ammonia are discharged into a closed water storage (reservoir). Analysis shows that the water contains nitrites and nitrates that are not present in the sewage waters flowing into the reservoir. Give the explanation of this phenomenon.

6. Why is sodium sulphite unsuitable for use in high-pressure boiler units?

Water Control
of Thermal Power Plants

7.1. Steam-Water Conditions
of Thermal Power Plant

Proper and reliable performance of a thermal power plant depends on thermal (furnace) and steam-water conditions under which it is intended to operate. The notion of the steam-water conditions is associated with all processes which take place in the steam-water circuit of a power plant. These processes arise from the action of water, steam, or impurities contained in steam and water. At electric power stations, steam-water conditions must be controlled so as to ensure trouble-free operation of thermal power equipment with no reduction in rated efficiency as a result of the deposition of sludge and scale in boiler units, on the blading of steam turbines, in condensers and other heat-transfer apparatus, and also due to corrosion of metal in boiler units, turbine and other equipment. To fulfil this requirement, it is necessary to follow all the recommendations and suggestions described above in different sections of the book. Usually, this involves a whole set of undertakings that must be carried on systematically. It is well known from practical experience that preventive correction of all violations of the steam-water conditions must be preferred to measures taken to eliminate the damages caused by these violations. Such practice rapidly leads to the desired results and cuts down monetary and material expenditures. Also, to ensure correct and reliable steam-water conditions for a thermal power plant, one must often take into account the demands of steam and water consumers. This is a problem that often faces industrial power generating facilities. Of importance here is the right approach to the problem. Thus, deferrization or deoiling plants are generally constructed to provide for a low concentration of iron or oil in industrial condensate. Meanwhile the concentration of these impurities can be reduced considerably by realizing simple

water-control measures. The construction of special facilities must only be contemplated where these measures prove insufficient. So, any irregularities in steam-water conditions must first be remedied by taking purely operational measures before deciding on the construction of special plants or on the reconstruction of facilities already in service.

7.2. General Requirements
for Chemical Control

Chemical control of water quality at an electric power station is aimed to timely detect the deviation of water-quality parameters from prescribed standards. So, chemical control must be expeditious, i. e. must provide for exact control data whenever necessary in order to decide on the measures to be taken to remedy the trouble. The objective of chemical control cannot be accomplished if this requirement is not fulfilled.

At electric power stations, chemical control is organized and carried out by the chemical department incorporating a chemical laboratory with its divisions, i. e. rough-analysis laboratories arranged in shops to conduct current operational control. The chemical laboratory itself is engaged in experimental-research activities dictated by operational requirements and exercises a more profound control of the processes and steam-water conditions and also supervises the work of the rough-analysis labs.

Chemical control of individual technological processes or processes in the sections of the water-treatment plant is conducted according to the instruction prescribing the following: the number of samples to be taken per shift, sampling schedule to be observed and water-, steam-, and condensate-quality parameters to be determined. Control is made possible by fitting where necessary sampling devices to take representative samples, i. e. samples reflecting correctly the quality of the flow from which the sample is taken.

Modern electric power stations operate under such steam-water conditions that concentrations of individual substances in the steam-water cycle are kept to a minimum. That is why rather strict requirements are imposed on the water control program. The methods of analysis applied must be highly precise, sufficiently simple and must require little time in performing the analysis. The accuracy of a method of analysis is characterized by the magnitude

of error δ in respect to the true value of the quantity being determined:

$$\delta = \frac{C' - C''}{C'} 100 = \frac{\Delta C}{C'} 100 \text{ per cent} \tag{7.1}$$

where C' and C'' are the true and the determined concentration of the substance of interest in the analyzed sample.

By the degree of accuracy of the method is meant here the minimum concentration of a given substance that can be determined with certainty by this method. With a given degree of accuracy of the method, the relative error will be smaller at an increased concentration of the substance of interest, C'. If the latter exceeds but little the concentration C'', then the result of analysis is inaccurate. One proceeds then in two ways: either a new, more accurate method of analysis is applied, or the concentration of the substance in the sample is increased somehow. The latter method of increasing the accuracy of analysis is widely practiced. The artificial increase in the concentration of substances in a sample is referred to as *sample enrichment*.

7.3. Water and Steam Sampling

It is not difficult to take samples from homogeneous media such as feedwater, chemically treated water, and condensate, since many sampling techniques yield rather representative samples reflecting the quality of the flow from which they are taken. Samples of chemically treated water and condensate are usually taken for the purpose of complete analysis by a probe or sampler of the kind illustrated in Fig. 7.1. If the temperature of water is high (> 313 K), the sample is placed in a refrigerator. Many samples of water and condensate are taken periodically. The quality of the water during the sampling interval remains then unknown. If this shortcoming is to be remedied, continuous average sampling is organized per shift or day, etc., or automatic control and recording is ensured. It is difficult to take representative samples from a heterogeneous medium such as saturated steam, since droplets of boiler water are nonuniformly distributed in the steam flow. Because of this a sample may contain mainly steam (improved sample) or chiefly droplets of boiler water (deteriorated sample).

At a small flow velocity, dry steam moves in the middle of the
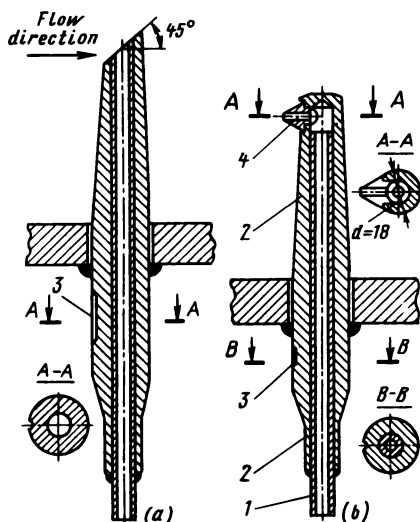
Fig. 7.1. Feedwater samplers

(a) tubular; (b) single nozzle; *1* — sampling tube; *2* — union; *3* — setting guide mark; *4* — nozzle

tube and the moisture entrained by it forms on the tube wall a film moving together with the steam. This pattern of flow persists until the flow acquires some velocity, said to be *critical*, at which the film of moisture is stripped off the wall and broken up into fine droplets that are entrained by the flow. The critical velocity of steam depends on pressure. At a steam pressure from 4.0 to 14.0 MPa, the steam velocity at which the moisture film is stripped off the wall falls within 2 to 4 m/s. For complete stripping of the film, it is required that the steam velocity in a pipeline should exceed the critical velocity 5 or 6 times.

The main steam sampler is a slotted probe depicted in Fig. 7.2. A row of holes *3* is arranged along the generating line of tube *1*. Two plates *2* soldered along the holes and adjacent to them form a slot. The steam sampling tube is inserted into a steam pipeline so that the slot faces the steam flow. If the velocity of steam in the pipeline, $v_s > 6v_{cr}$, then samples are taken with the aid of the slotted probe without any supplementary devices, since in this case moisture will be uniformly distributed over the steam flow. At $v_s <$
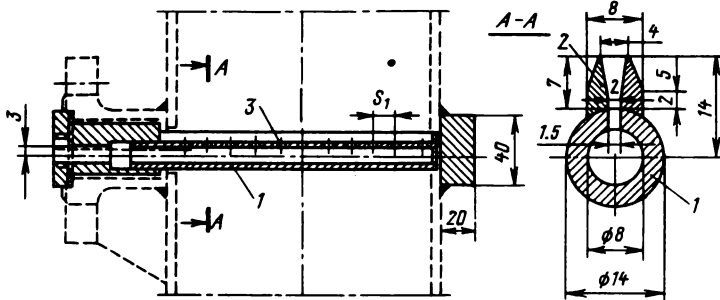
Fig. 7.2. Slot-type sampler
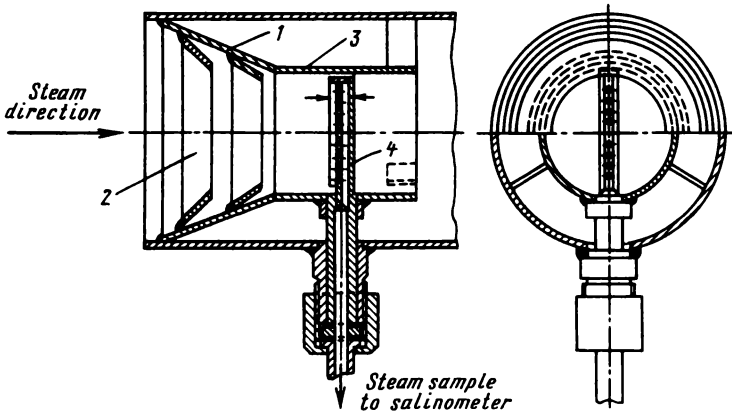
Fig. 7.3. Device for taking average steam samples, with a mixer

$< 6v_{cr}$, there is a need for a special device to strip the moisture film off the wall; a special mixing device used for this purpose is illustrated in Fig. 7.3. Truncated cone *1* fitted inside a steam pipeline has several taper rings *2* fixed over its length. The smaller base of cone *1* is secured to tube *3* in which slotted probe *4* is mounted. The steam-entrained film of moisture runs onto the taper rings and is torn away from their edges by the steam flow. The steam velocity in tube *3* is above the critical value and moisture is in atomized state. This method of steam sampling has an advantage
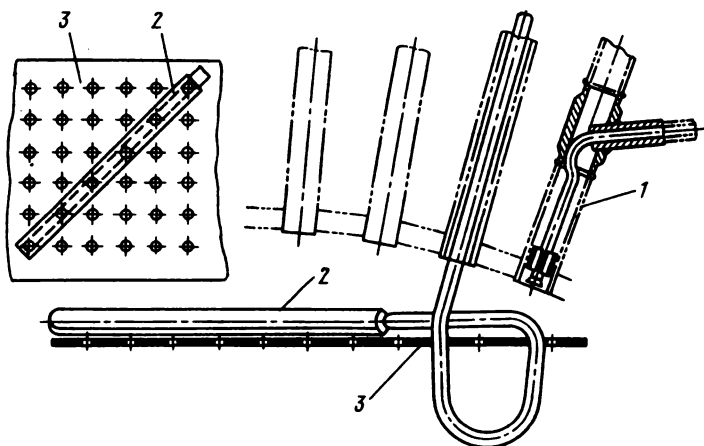
Fig. 7.4. Saturated steam sampling devices

l — mouth-type steam sampling device placed in a steam outlet tube; *2* — slot-type steam sampler placed in the steam space of a boiler drum; *3* — perforated plate

over other methods, especially at elevated loads of the boiler unit, in which case the steam wetness increases.

If steam leaves a boiler drum through small-diameter tubes, where installation of a mixer or probe of the kind shown in Fig. 7.2 is hampered, mouth-type probes are used. Various designs of steam sampling devices are shown in Fig. 7.4. The composition of a sample will represent the composition of the main flow if the steam inlet velocities are almost the same for the two tubes. Therefore, the bell-mouthed end of the probe tube is set in the plane of location of the initial length of the steam outlet tube. The second variant shows how samples are taken directly in a drum by means of a slot-type probe. The sample taken is placed in a refrigerator for condensation or is examined for salt content on a salinometer.

7.4. Thermochemical Testing of Boiler Units

It is usually natural-circulation boiler units that are in need of thermochemical tests. Water conditions of a drum-type boiler unit are determined by three quantities: steam load D_s, level of boiler water in the drum, h_l, and the concentration of substances in boiler

water, S_{bw}. The maximum admissible values of these quantities must be known to the attending personnel so as to ensure dependable performance of the boiler unit and turbine. These values cannot be calculated and are usually specified after conducting thermochemical tests.

The objective of these tests consists in determining dependences $S_s = f(D_s)$, $S_s = f(h_l)$, $S_s = f(S_{bw})$ for a given boiler unit, which specify the maximum admissible values of D_s, h_l and S_{bw}. For the purpose of thermochemical testing, the boiler unit is fitted with all necessary boiler-water and steam samplers and instrumentation.

First, the effect of steam load on steam quality is investigated, with boiler water kept at a middle level and with a somewhat decreased salt content. For this, the boiler is tested under three or four loads in succession up to the maximum admissible load. Test duration under each load is 5 to 7 h. Next, the admissible salt content of boiler water is determined. The tests are conducted with water kept at a middle level and the boiler unit operated under a rated load. The concentration of salts in boiler water is increased stepwise up to critical values. The rate of increase in salt concentration is taken equal to about 50-70 mg/l h for primary sections and 300 mg/l h for secondary sections. The test lasts 5 to 7 h with every increase in salt concentration. Having found the maximum boiler-water concentration, steam quality is checked, with drum water being raised to the highest admissible level.

Water conditions for once-through boilers are specified by the quality standards prescribed for feedwater. That is why, instead of testing, the entire water-steam-condensate circuit of a plant is adjusted for operation under certain conditions.

7.5. Quality Standards for Feedwater, Boiler Water, Steam and Condensate

By the quality standards prescribed for water and steam are meant the maximum hardness, alkalinity, salt content, silicon content, and concentration of metal corrosion products and gases above which the formation of deposits or corrosion becomes possible. Calculated and operational standards are distinguished. Calculated quality standards are used in designing water-treatment plants or drum internals. Operational quality standards are usually specified by conducting special tests on a boiler unit or

a water-treatment plant, or are based on generalization of operational data.

Both calculated and operational standards must meet the requirements of adopted rules for construction and safe operation of steam and water-heating boiler units and rules for technical maintenance of electric power stations and heat-distribution systems.

The rules for construction and safe operation of steam and water-heating boilers, to be observed by all USSR industrial enterprises and services, contain a number of requirements and standards that stipulate water conditions for boiler units operated at pressures up to 3.9 MPa. According to these rules, it is required to secure normal operation of a boiler without damage to its component elements due to deposition of scale, sludge or as a result of corrosion. Quality standards for feedwater and boiler water and also continuous-blowdown and intermittent-blowdown rates must be established for boilers of a capacity of 0.7 t/h and over.

The quality of feedwater for natural-circulation boilers rated 0.7 t/h and above and intended to operate at pressures up to 3.9 MPa must satisfy the following requirements.

For gas-tube and fire-tube boilers, the total hardness is not greater than 500 μg-equiv/kg when operated on solid fuel, and not over 30 μg-equiv/kg when operated on gas and oil. For water-tube boilers operated at a pressure not higher than 1.3 MPa and 1.3 to 3.9 MPa, the total hardness is 20 μg-equiv/kg and 15 μg-equiv/kg, respectively.

The concentration of dissolved oxygen is as follows: for boiler units operated at 3.9 MPa with an output of not less than 2 t/h and having no steel economizers, it is not over 100 μg/kg, and for boiler units fitted with steel economizers not over 30 μg/kg. For boiler units operated at a pressure up to 1.3 MPa, the oil content of feedwater is no more than 5 mg/kg, and for boiler units of 1.3 to 3.9 MPa it is less than 3 mg/kg.

Rules prescribe that the quality of feedwater for steam boilers operated at a pressure over 3.9 MPa and also for once-through boilers irrespective of operating pressure should meet quality standards for feedwater and steam given below in Tables 7.1 through 7.3.

The hardness of water for spray-type desuperheating should be not over 3 μg-equiv/kg for natural-circulation boilers and not over 0.2 μg-equiv/kg for once-through boiler units; the concentration of

Table 7.1

Feedwater Quality Standards for Natural-Circulation Boiler Units

Water quality characteristic	Pressure, MPa			Application conditions
	≤4.0	4.0-10.0	>10.0	
Hardness, μg-equiv/kg	≤5	≤3	≤1	When oil is fired
	≤10	≤5	≤1	Other kinds of fuel
SiO_2 content, μg/kg	–	≤80[1]	≤40	For regional electric-power stations and heating and power plants[2]
O_2 content, before deaerator, μg/kg	≤30	≤30	≤30	Before deoxygenation reagents are introduced
Same, after deaerator	≤20	≤20	≤10	
Na_2SO_3 content before economizer, mg/kg	≤2	–	–	Sulphite treatment
N_2H_4, μg/kg	20-60	20-60	20-60	Hydrazine treatment
pH value (at 298 K)	9.1 ± 0.1	9.1 ± 0.1	9.1 ± 0.1	
CO_2 content		Absent		After deaerator
NH_3 content, μg/kg	≤1000	≤1000	≤1000	
NO_2 content, μg/kg	–	≤20	≤20	
$NO_2^- + NO_3^-$ content, μg/kg	–	≤20	≤20	For pressures >6.0 MPa
Fe content, μg/kg	≤100	≤50	≤20	When oil is fired
	≤200	≤100	≤30	Other kinds of fuel[3]
Cu content, μg/kg	≤10	≤10	≤5	When oil is fired, for 3.0 to 10.0 MPa
	≤20	≤20	≤5	Other kinds of fuel, for 3.0-10.0 MPa

Table 7.1 (continued)

Water quality characteristic	Pressure, MPa			Application conditions
	≤ 4.0	4.0-10.0	> 10.0	
Oil content, mg/kg	≤ 1	≤ 0.3	≤ 0.3	

Notes. 1. For pressures from 7.0 to 10.0 MPa.
2. For heating and power plants with industrial steam extraction, SiO_2 concentration is specified on the basis of test results; for pressures above 10.0 MPa, it is over 120 µg/kg.
3. For boiler units operated at pressures ≥ 14.0 MPa, Fe concentration is taken below 20 µg/kg.

Table 7.2

Quality Standards for Feedwater of Once-Through Boiler Units

Water quality characteristic	Magnitude	Application conditions
Content of sodium compounds (taken as sodium content), µg/kg	≤ 5	—
SiO_2, µg/kg	≤ 15	—
Total hardness, µg-equiv/kg	≤ 0.2	—
Fe, µg/kg	≤ 10	—
Cu, µg/kg	≤ 5	Before deaerator
O_2, µg/kg	≤ 30	Same
	≤ 10	After deaerator
pH value (at 298 K)	9.1 ± 0.1	—
Conductivity at 298 K, µS/cm	≤ 0.3	—
Excess N_2H_4, µg/kg	20-60	—
Content of oil and oil products, mg/kg	≤ 0.1	—

Fe and Cu should not exceed the values stipulated by quality standards for feedwater; the concentration of sodium and SiO_2 components must be such that the quality of superheated steam should meet the prescribed standards.

Table 7.3

Quality Standards for Steam Generated in Natural-Circulation Boiler Units

Steam Quality Characteristic	Pressure, MPa			Prescribed for
	$\leqslant 4.0$	4.0-10.0	> 10.0	
Sodium compounds $\leqslant 60$ (taken as Na), µg/kg		$\leqslant 15$	$\leqslant 10$	District electric power stations and heating and power stations
	$\leqslant 100$	$\leqslant 25$	$\leqslant 15$	Heating and power stations with process steam extraction
Content of SiO_2, µg/kg	–	$\leqslant 15$	$\leqslant 15$	District electric power stations, $p \geqslant 7.0$ MPa
	–	$\leqslant 25$	$\leqslant 25$	Heating and power stations, $p \geqslant 7.0$ MPa

Note. For district electric power stations fitted with once-through boiler units operated at all pressures specified, the admissible content of sodium in steam is not over 5 µg/kg.

Table 7.4

Quality Standards for Makeup Water of Heat-Distribution Systems

Water quality characteristic	System water heating temperature, K		
	$\leqslant 348$	349-423	424-473
Dissolved oxygen, µg/kg	$\leqslant 100$	$\leqslant 50$	$\leqslant 30$
Suspended solids, mg/kg	$\leqslant 5$	$\leqslant 5$	$\leqslant 5$
pH value (at 293 K)	–	6.5-9.5	6.5-9.5
Carbonate hardness, mg-equiv/kg	$\leqslant 1.5$	$\leqslant 0.7$	$\leqslant 0.4$
Total hardness, mg-equiv/kg*	–	$\leqslant 0.05$	$\leqslant 0.05$

* When boiler blowdown water is used (admissible in closed circuit heat-distribution systems).

For natural-circulation boiler units operated at a pressure of 4.0, 4.0 to 10.0, and over 10.0 MPa, the hardness of turbine condensate must be not over 10, 5, and 1.0 μg-equiv/kg, respectively. For once-through boiler units, it should not exceed 0.5 μg-equiv/kg.

The concentration of O_2 in the condensate delivered by condensate pumps should not exceed 20 μg/kg.

Quality standards for boiler water and blowdown rates must be established based on thermochemical testing. Makeup water for heat-distribution systems must meet the quality standards given in Table 7.4.

If at an electric power station fitted with subcritical-pressure once-through boiler units no facilities are provided for treating all the condensate discharged from condensers, feedwater may contain up to 10 μg/kg of sodium compounds and up to 20 μg/kg of iron compounds; the total hardness must not exceed 0.5 μg-equiv/kg.

Chapter 8

Removal of Coarse-Dispersed and Colloidal Impurities from Water

8.1. Clarification of Water

By *clarification* is meant the removal of coarse-dispersed and colloidal impurities from water. Coarse-dispersed solids may be removed from water by *sedimentation* and *filtration*.

When clarified by sedimentation, solid particles settle by gravity on the bottom of a settling tank in which the water undergoing clarification is at rest or in slow horizontal or upward motion. Thus, it is only the particles which sink in water that can be removed from it by sedimentation. Sedimentation takes a long time, requires large-capacity settling tanks and cannot ensure complete removal of coarse-dispersed impurities from water. That is why sedimentation is never practiced as the only means of clarification in preparing makeup water at electric power stations.

Filtration is a process of clarification of water by passing it through a porous material, which retains coarse impurities on its surface and in pores. An apparatus used for filtration is called a *filter* and the porous material that fills the filter is known as the *filtering medium* or *filtering material*. Filters used for water clarification are termed *clarifying filters*, sometimes referred to as *mechanical filters*.

Filtration of water is due to the difference between pressures at the top of the bed of filtering material and underneath it. The difference Δh is called the pressure drop through the filtering bed. The quantity Δh usually denotes not only the pressure drop through the filtering material, but also the drop in pressure through the filter proper (in the distribution devices, pipelines, etc.)

The pressure drop through the filtering bed (also known as the resistance offered by that bed to water flow) depends on the rate of filtration, height of the filtering bed, diameter (size) of grains of the filtering material and the degree of its contamination by the trapped impurities. Greater numerical values of these factors (except

grain size) result in a greater pressure drop Δh. Of the enumerated factors, only contamination of the filtering bed increases continuously, which causes an increase of the pressure drop from some minimum, Δh_0, corresponding to a clean bed of filtering material, to the maximum admissible value, $\Delta h_{max} = (0.8$ to $1.0) \times 10^5$ Pa for pressure filters and $(0.2$ to $0.3) \times 10^5$ Pa for open filters. The rate of water filtration in mechanical filters, v, is assumed within 5 to 10 m/h.

When contamination of a filter cannot be tolerated any more, it is taken out of service for subsequent washing, in the course of which the impurities trapped in the filtering bed are washed out. Then the filter is again put into service. The time a filter is kept in service between two successive washings is called the *working period*, or *filter run*. It is desirable to keep a mechanical filter in service as long as possible, but not less than 8 h. The duration of the filter run depends on many factors, of which one must mention the concentration of suspended solids in the filtered water, C_{ss}, and the *mud capacity* of a filter, $T = Mh/C_{ss}v$. The mud capacity of a filter, M, is the quantity of impurities entrapped in the filter during the filtering period, related to 1 m³ of the filtering material and expressed in kilograms. The greater the mud capacity of a filter at a given C_{ss}, the longer the duration of the filter run. If water in the amount of Q has been passed through a filter, then

$$M = \frac{QC_{ss}}{10^3 \, hf} \tag{8.1}$$

where h = height of filtering bed, m
f = filter cross-sectional area, m²
Q = amount of water filtered, expressed in m³

The filtering materials used are crushed anthracite (piece size 0.8-1.5 mm); quartz sand (0.5-1.0 mm grain size) containing no more than 96 per cent SiO_2; porous clay (0.8-1.5 mm piece size). It must be borne in mind that quartz sand dissolves in alkaline water, enriching the filtered water (often called filtrate) with silicic acid.

8.2. Design of Mechanical Filters with Granular Beds

Mechanical filters of different types and designs are shown schematically in Fig. 8.1. The single-flow (single-bed) closed pressure filter *1* is of the simplest construction. A certain part of its

volume is filled with the material constituting the filtering bed on top of which the filter is filled with water called the *water cushion*. Closed pressure filters operate under the pressure created by the pumps delivering the water to be clarified.

In open-type mechanical filters *2* filtration is due to the pressure exerted by the column of water *h* in the filter. Filters of this kind find wide application in plants engaged in purification and treatment
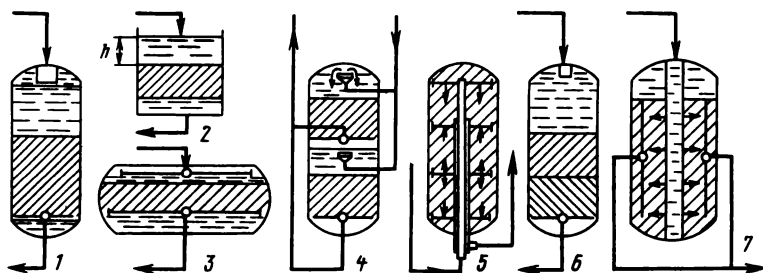
Fig. 8.1. Clarifying filters

1 — single-flow; *2* — open; *3* — horizontal-flow; *4* — two-chamber; *5* — three-flow; *6* — two-bed; *7* — radial-flow

of drinking water. The rectangular cross-section filters are constructed from reinforced concrete with a large filtering surface. The comparatively small head *h* restricts operation of these filters at increased filtering rates.

Horizontal closed pressure filters *3* have a large filtering surface and, consequently, a large throughput per filter. They are, however, cumbrous and require much floor space when installed indoor. Multiflow mechanical filters *5* are free of this demerit. They are filled completely with the filtering material, inside which the draining and distributing devices are arranged. It is clear from the schematical representation of filters of this kind that they permit the water to be passed in several flows (three in the illustration) and make it possible to increase the output of a filter as many times.

Chamber-type filters *4* are separated into chambers by solid partitions (into two chambers in the illustration). The chambers serve as two ordinary single-bed filters operated in parallel.

To increase the rate of filtration, improve the quality of clarified water, and raise the mud capacity of filtering material, single-flow

filters are often charged with two filtering materials of different bulk mass and grain size, for instance, crushed anthracite (0.8 to 1.6 mm grain size) and quartz sand (0.5 to 1.0 mm grain size). The sand, being a denser material, is arranged underneath the anthracite filtering bed. Two-bed filters of this kind *6* are often used in practice.

In radial-flow filter *7* the filtering material is charged into the annulus formed between the filter shell (wall) and an internal tube. The water treated is delivered into the central tube which distributes it through the filtering material heightwise. Water is passed in radial flows through the filtering material.
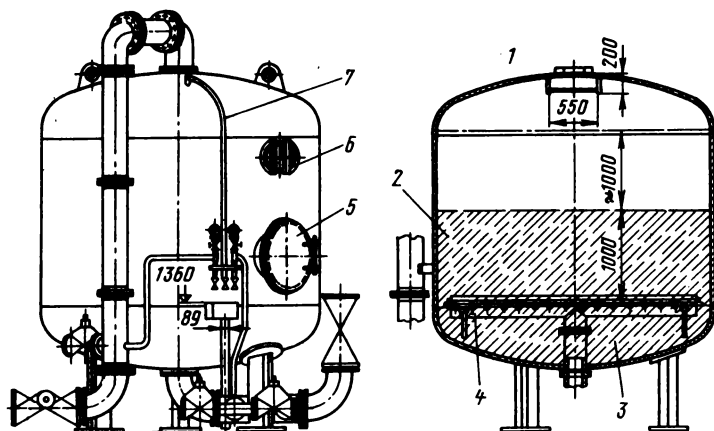
Fig. 8.2. Clarifying filter

The most common type of clarifying filter is a single-flow, single-bed, pressure filter illustrated in Fig. 8.2. The filter is built up of a cylindrical shell and ellipsoidal heads and is designed for an operating pressure of 0.6 MPa. Space *3* in the bottom head of the filter can be filled with concrete or filtering material *2* to form a bed 1 m thick, measured from the lower distributing device *4* upwards. Perforated distributing device *1* and air vent pipe *7* are arranged in the top part of the filter. Two manholes *5* and *6* permit access into the filter for inspection and repairs.

The main piping of the filter is shown in Fig. 8.3. Water enters

the filter through valve *1* and flows downward through the filtering bed. The clarified water (filtrate) leaves the filter through valve *7*. Backwash water is delivered at the bottom through valve *5* and discharged from the filter into the sewerage through valve *8* together with the washed out impurities. Valve *6* is used to drain off water. Compressed air is delivered through connection *4*. Valve *3* permits discharge of the material. The most important component of the clarifying filter is underdrain system 9 ensuring uniform distribution of water over the filter's cross-sectional area and also preventing carry-over of the filtering material from the filter.

Two designs of underdrain systems are presently available. Filters
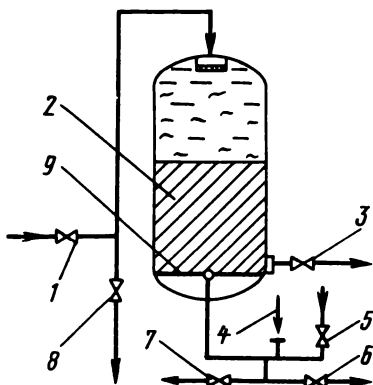
Fig. 8.3. Schematic of a clarifying filter

up to 1400 mm in diameter are fitted with an underdrain system of the "false bottom" type (Fig. 8.4). At the bottom the filters (1 m in˙ diameter) have flange joint *1*. Round, strong perforated plate *3* made from a polymer material is clamped between the flanges. Slotted caps *2* are fitted in the perforations in plate *3*.

Filters from 2 to 3.4 m in diameter are fitted with a lateral type underdrain (Fig. 8.5). It consists of header *1* to which lateral distributing arms (pipes) *5* are connected. Holes *3* provided in each distributing arm are covered by trough *4* secured to the arm by spot welding. Along each trough there are 0.4 mm slots. Lateral arms *5* are fastened to angles *7* by means of bolts *8* and shackles *6* welded to the arms. Angles *7* are rigidly fixed in the bottom head of the clarifying filter. When a nut is tightened on bolt *8*, taper end
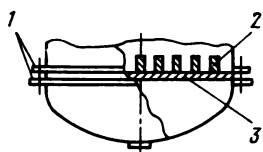
Fig. 8.4. Underdrain system of the "false bottom" (deflector-plate) type
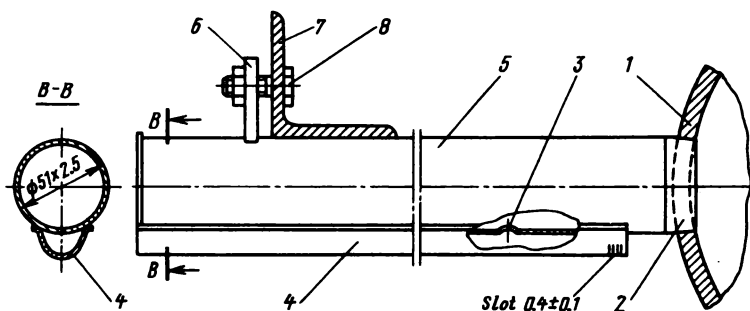
Fig. 8.5. Component element of underdrain system of the header-lateral type
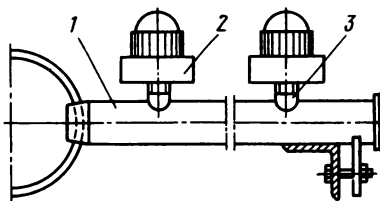
Fig. 8.6. Component element of underdrain system with strainers

2 of the lateral arm is pressed to the header, thereby ensuring a reliable air-tight joint. In mechanical filters the lateral distributing arms are arranged so that the troughs face downward.

Figure 8.6 illustrates an underdrain system of the header-lateral type with strainers *2* secured on connection *3* welded to lateral arm *1*.

8.3. Design of Tubular-Element Precoat-Type Filters •

The clarifying filters with a granular filtering bed considered above have a high bed of course-grained filtering material and a small filtering surface. In contrast to these filters, tubular-element precoat-type filters feature a large filtering surface, thin filtering bed (5 to 10 mm thick), and mainly use powders as filtering materials.

A filter of this type and its piping are shown in Fig. 8.7. Cylindrical shell *1* with elliptical heads accommodates tube sheet *12*
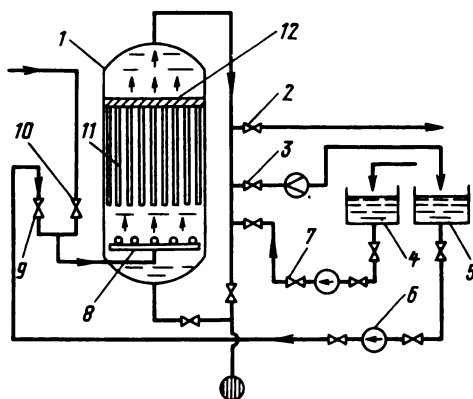
Fig. 8.7. Schematic of tubular-element precoat-type filter

to which tubular filtering elements *11* are secured. The tubular elements are available in a variety of designs, but all of them are made of a 30 to 50 mm dia tube with holes covered with polymer or metal mesh with 100 × 100 μm openings. Stainless wire is often wound on the tube with turns spaced 100 to 150 μm apart.

The filtering material (powdery or fibrous cellulose, ionite and perlite powders) is charged into tank *5* in the amount of 1 kg per m² of the surface of a filtering element, then the tank is filled with water and the mixture stirred until a homogeneous suspension is obtained. Pump *6* delivers the suspension through valve *9* to distributing device *8* of the filter. The suspension fills the filter and passes through the meshes of the filtering elements. Water leaves

the filter through valve *3* into tank *5*, while the material remains on the surface of the filtering elements and forms a filtering bed.

Recirculation of the suspension continues until the entire filtering material rests on the filtering elements. Pump *6* is then shut down, valve *9* closed, and the condensate or water to be clarified is permitted to flow into the filter through valve *10*. The water (or condensate) passes through the bed of filtering material, then through the tubes of filtering elements into the space over the tube sheat, and leaves the filter via valve *2* for further treatment. As the mud capacity of the filtering bed (layer) becomes exhausted, the filtering material is washed off and removed from the filter. For this purpose wash water is delivered by pump *7* from tank *4* inside each filtering element (at the top of the filter). Leaving the filtering elements, the water washes off the layer of the filtering material and entrains it into the drain. After that another filtering cycle is initiated and all the operations described above are repeated in the same sequence.

Tubular-element precoat-type cellulose filters find application in condensate treatment plants of modern boiler-turbine units to remove mainly metal corrosion products from the turbine condensate. They are connected to the system upstream of mixed-bed (monobed) filters. Precoat-type filters are often used for the same purpose at steam and nuclear power stations. In this case a mixture of ionite-exchanger powders (КУ-2 and АВ-17 types) serves as a filtering material in filters. Precoat-type ionite-exchanger filters are capable of operating at temperatures up to 373-383 K, and therefore they can be used to purify hot condensate and water. These filters are considered promising for service in high-capacity steam generator-turbine units operated at nuclear power plants. A precoat-type filter with powdery perlite (porous SiO_2) used as a filtering material is suitable for fine clarification of water. A mixture of powdery perlite and activated carbon is used for removing oil from condensate.

The output of a precoat-type filter, m^3/h, is determined from the equality

$$q = vfm = v\pi dLm \tag{8.2}$$

where

$$m = \frac{\pi D^2}{4(l + d)^2 \times 0.86} \tag{8.2a}$$

Then the total surface of a tubular-element precoat-type filter is

$$F = fm = \frac{\pi^2 dLD^2}{4(l + d)^2 \times 0.86} \qquad (8.2b)$$

In formulae (8.2) through (8.2b),

v = rate of filtration, usually equal to 10 m/h
d = diameter of a tubular filtering element, m
D = diameter of precoat-type filter, m
m = number of tubular filtering elements
L = length of tubular filtering element, m
l = distance between generating lines of tubular filtering elements, m
f = surface area of tubular filtering element, m^2

Manholes not shown in the layout in Fig. 8.7 are used for installation of filtering elements, their removal and also for inspection of the filter.

8.4. Attendance of Clarifying Filters

The time of functioning of a filter comprises two periods: water filtration (working period), and filter washing (idling period). During the first period, attendance of the filter consists in controlling the degree of water clarification, which is characterized by transparency, the rate of filtering, and the pressure drop (resistance to water flow) through the filter. To make such attendance possible, the filter is fitted with a clarified-water flow meter and two pressure gauges to which pressure is tapped from the pipelines of clarified water and water being clarified. The filter is taken out of service for washing if the pressure drop reaches the preset limit, or deterioration of water clarification is observed. These two factors rarely coincide. The filter ·is taken out of service by closing valves *1* and *7* (see Fig. 8.3).

Washing of filters is accomplished by passing wash water through the filter from the bottom. For this purpose valve *5* is opened, then valve *8* is opened smoothly until the rate of wash water flow through the filter becomes sufficient to wash out impurities. This rate of flow is characterized by the intensity of washing, i_w, l/m^2 s, expressed in litres of water passing in one second through 1 m^2 of filter surface. The magnitude of i_w depends on the kind of filtering material, its grain (piece) size, and the rate of wash water flow. For

quartz sand, i_w = 12 to 15 and for crushed anthracite 7 to 8 l/m² s. If the intensity of washing is too high, the water can entrain the filtering material into the sewerage; on the other hand, washing of low intensity will fail to serve the purpose.

Counterflow washing causes the filtering material to expand; material particles then begin to move in the ascending water flow, which aids in better washing out of impurities. The efficiency of washing is often raised by delivering compressed air into the filter through union 4 for 3 to 5 min at a rate of 15 to 20 l/m² s for quartz sand and 10 to 15 l/m² s for crushed anthracite.

Washing of a filter is usually conducted for 6 to 10 min, then valves 5 and 8 are closed and valves 1 and 6 opened. The filter is kept open to the drain for several minutes to dispose of the first portions of turbid water. This operation can be omitted if the first filtrate is sufficiently transparent. As soon as clarified water transparency becomes normal, valve 6 is closed and the filter is put into service by opening valve 7.

The output of one filter, m³/h, is determined by the formula

$$q = vf \tag{8.3}$$

The capacity of a filtering plant, comprising m filters, can be expressed in terms of the amount of water passed through the filters (gross capacity Q_g) or the amount of clarified water that finds useful application (net capacity Q_n). The quantity $\Delta Q = Q_g - Q_n$ characterizes the amount of water covering the boiler house needs. The capacities Q_q and Q_n are determined by means of flow meters. In designing filtering facilities, Q_n can be calculated by the formula

$$Q_n = mvf\left(\frac{24 - n_w\tau_w}{24}\right) \tag{8.4}$$

where n_w = number of washings of each filter per day
       τ_w = time during which filters are kept idling for washing, h

The amount of water, m³, used for one washing of a filter

$$g = \frac{3.6i_w ft}{60} \tag{8.5}$$

whence

$$\Delta Q = \frac{qmn_w}{24} \tag{8.6}$$

and

$$Q_g = Q_n + \Delta Q \qquad \bullet \qquad (8.7)$$

where t is the duration of washing (6-10 min).

8.5. Coagulation of Water

8.5.1. *Essence of the Process*

Coagulation is the process of consolidation (conglomeration, adhesion, clotting) of colloidal particles, terminating in precipitation of the substance removed from the treated water by means of settling or filtration. The opposite process, i.e. the transition of a solid (such as a deposit) into a colloidal state, is called *peptization*. In water-treatment technology, under coagulation is understood the treatment of water with special reagents so as to remove colloidal and coarse-dispersed impurities.

Since colloidal solutions are very stable, colloidal particles are incapable of spontaneous consolidation into coarse (large) formations and precipitation from a solution in the absence of suitable stimulants. The reason is that colloidal particles of a given substance carry like charges which prevent the consolidation of particles.

The most effective method of removing these charges is mutual coagulation of two colloids whose particles are oppositely charged. Reagents that are able, upon introduction into water, to provoke coagulation of natural colloids are called *coagulants*.

Some time after introduction of a dose of coagulant into a sample, the water becomes turbid. Turbidity increases with time, and gradually large flakes form and start settling on the bottom of the vessel, entraining all the impurities. The visible result of coagulation is the formation of a deposit in the form of porous gelatinous flakes that settle on the bottom of the vessel. If this is not observed, no coagulation takes place in the vessel.

In water-treatment practice, ferrous iron sulphate, $FeSO_4 \cdot 7H_2O$, aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, iron chloride, $FeCl_3$, are used as coagulants. They are introduced into water in solutions of 5 to 10 per cent concentration. When a coagulant such as aluminium sulphate is introduced into water, it first undergoes hydrolysis according to the following formula

$$Al_2(SO_4)_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 3H_2SO_4$$
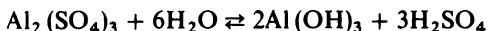
The acid being formed is neutralized due to water alkalinity

$$H^+ + HCO_3^- \rightarrow CO_2\uparrow + H_2O$$
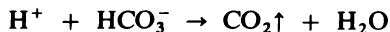
These processes also take place if ferrous iron is introduced into water instead of aluminium sulphate, $Al_2(SO_4)_3$:

$$FeSO_4 + 2H_2O \rightleftarrows Fe(OH)_2 + H_2SO_4$$

$$H^+ + HCO_3^- \rightarrow CO_2\uparrow + H_2O \left. \right\}$$
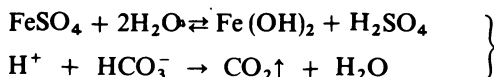
It is not $Fe(OH)_2$ that acts as a coagulant, but ferric hydroxide, $Fe(OH)_3$. So, when ferrous iron is used as a coagulant, the need arises to oxidize it into ferric iron by oxygen dissolved in water:

$$2Fe(OH)_2 + {}^1/_2O_2 + H_2O \rightarrow Fe(OH)_3$$
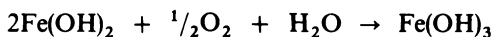
This reaction proceeds rather easily in an alkaline medium.

The foregoing reactions indicate that water alkalinity decreases upon coagulation and the concentration of free carbon dioxide in water increases. For this reason the water being treated with coagulants must contain some minimum amount of alkaline substances, mg-equiv/kg, specified by the following equation

$$A_{min} = d_c + 0.4$$

where d_c is the dose of coagulant, mg-equiv/l.

If the actual alkalinity of the coagulant-treated water, $A_t < < A_{min}$, alkalis such as NaOH, Na_2CO_3, $Ca(OH)_2$ must be introduced into the water in the amount

$$A_c = d_c + 0.4 - A_t$$

Since coagulant-treated water shows increased transparency and decreased oxidizability, it is these characteristics that are used in exercising control and evaluating the efficiency of coagulation.

In carrying out coagulation procedures, it is expedient to provide for precipitation of a maximum fraction of the coagulant with its subsequent removal in clarifiers or clarifying filters. Otherwise, it can lead to an inadmissible contamination of the ion-exchange material and penetration of iron or aluminium into boiler units. It is therefore essential to create conditions in which the coagulant introduced into water would be completely hydrolyzed attended by the formation of difficultly soluble hydroxides.

The process of coagulation is very sensitive to the conditions in which it takes place. It is affected by the pH value of the medium,

amount of the coagulant introduced, water temperature, etc. The effect of the pH value makes itself felt heavily when water is treated with aluminium sulphate. As follows from the hydrolysis reaction

$$2Al^{3+} \quad + \quad 6H_2O \quad \rightleftarrows \quad 2Al(OH)_3 \quad + \quad 6H^+$$
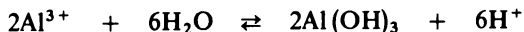
an increase in hydrogen-ion concentration, i.e. a decrease in the pH value of water, causes the equilibrium of this process to shift to the left. When pH is sufficiently low, $Al(OH)_3$ passes into the solution and the process of coagulation is disturbed. Aluminium hydroxide dissolves even at a rather high pH value ($\geqslant 8$), resulting in the formation of aluminates according to the formula

$$Al(OH)_3 \quad + \quad NaOH \quad \rightarrow \quad NaAlO_2 \quad + \quad H_2O$$
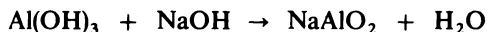
This coagulant must not be applied where pH of water exceeds 8, as is the case in water-treatment plants using lime. It should be replaced by ferroferric compounds, which coagulate successfully even at pH above 8.

The pH value of the water to be treated and the coagulant to be used are specified by laboratory analyses. When aluminium compounds are used, pH may be assumed to be within 5 to 7; with iron compounds used, it is within 8 to 10. Aluminium sulphate is taken in an amount of 0.2 to 1.0, and ferrous oxide 0.1 to 0.5 mg-equiv/l. The most favourable temperature of coagulant-treatable water is 303-313 K.

8.5.2. Polyelectrolytes (Flocculators)

In recent years substances referred to as flocculators or polyelectrolytes have found wide application. These are organic high-molecular compounds which comprise many ionogenic groups. When dissolved in water, these groups undergo ionization, in the course of which the radical proper (molecule) becomes positively charged in some polyelectrolytes (cation-exchange flocculators) and negatively-charged in others (anion-exchange flocculators). Of these substances, two flocculators, polyacrylamide (weak anion-exchange flocculator, type ПАА) and the BA-2 flocculator (of the cation-exchange type) have found practical application in the USSR.

When polyacrylamide is introduced into water that already contains coagulant flakes or precipitating suspension, the flakes consolidate and gain weight, which accelerates their settling. Polyacrylamide alone does not induce coagulation of colloids and

the formation of suspension. But being sorbed by particles of the suspension, polyacrylamide "sews them", as it were, and forms a net structure that aids in the formation of large flocs (large particles). These flocculent aggregations are denser and heavier than individual particles and settle out quicker. Polyacrylamide (an 8 per cent solution) is available in a gelatinous white mass. It dissolves in water, provided that intensive stirring is ensured, and is used as a solution of a 0.1 or 0.2 per cent concentration. The chemical is introduced in doses ranging from 0.5 to 2.0 mg/l.

The BA-2 polyelectrolyte is used without any coagulant since the chemical itself brings about coagulation of colloids. Most of the colloidal particles carry negative surface charges, but the molecules of the BA-2 chemical are positively charged. That is why mutual neutralization of the charges takes place, resulting in that a molecule of the flocculator is sorbed by particles of the suspension being formed together with coarse aggregates and complexes that accelerate the suspension settling in the coagulation tank. The polymeric flocculator, type BA-2, is a slightly viscous yellow liquid at an 11 per cent concentration. The dose of the chemical to be introduced depends on the concentration of suspended substances and does not exceed 1.0 to 1.5 mg/1 with a concentration of suspended solids reaching 10 to 180 mg/l. The BA-2 type polyelectrolyte, taken in increased dosages, can also be used successfully in treating coloured waters.

8.5.3. Preparation of Coagulant Solutions

The consumption of coagulant, kg/h, corrected to anhydrous substance, is calculated by the formula

$$g_c = \frac{Q_g d_c E_c}{1000} \qquad (8.8)$$

The commercial product contains C_c, %, of pure substance, so that the amount of product consumed must be $100/C_c$ times the amount of pure coagulant. The volume of the working solution, expressed in l/h, of concentration C (in mass per cent, see formula 1.1), which corresponds to the amount of g_c, is

$$V_s = \frac{g_c 100}{\rho_s C} \qquad (8.9)$$

The quantity of alkali, g_a, kg/h, spent on water alkalization, whenever necessary, is calculated by the formula

$$g_a = \frac{Q_g \Delta A E_c}{1000} \tag{8.10}$$

The solutions of easily-soluble reagents (coagulants, alkalis, phosphates) for small-capacity plants are usually prepared in special mixing tanks (Fig. 8.8). The measured (weighed) quantity of reagent, G_c, is charged into mixer *1* filled to two thirds of its working space
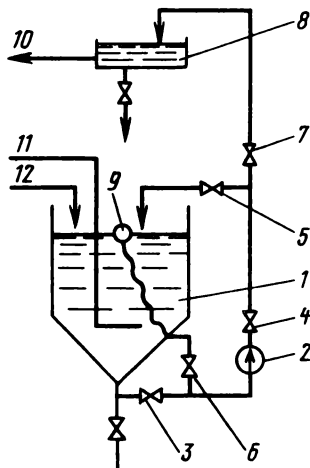
Fig. 8.8. Layout of mixing tank for preparing solutions of easily soluble chemicals

with water *12*. To initiate mixing *(stirring)* of the solution, valves *3*, *4*, and *5* are opened, and pump *2* is switched on. The pump draws the solution at the bottom and returns it into the mixer. To speed up the dissolution of the reagent, the solution can be heated by supplying steam *11* into the mixer. After stirring the solution for 15 to 30 min, the pump is switched off, valves *3* and *5* are closed, and the solution is given time for settling. The clarified solution is pumped into distributer tank *8*, from which it is fed to metering devices through pipeline *10*. Valves *6*, *4*, and *7* must be kept open during pumping.

If the working space of mixer is V_m, m³, and it is necessary to

prepare a solution with concentration C (in mass per cent), then the mixer must be charged with the following amount of anhydrous reagent, kg:

$$G_c = \frac{V_m 10^3 \rho_s C}{100} \tag{8.11}$$

The prepared amount of the solution will ensure continuous operation of a coagulation plant during the time, h,

$$t = \frac{V_m 10^3 \rho_s C}{100 g_c} \tag{8.12}$$

To preclude entrainment of the sludge settled on the bottom of the mixer, the pump's suction connection must be suspended from float 9. There is no need in doing it when the reagent does not contain impurities.

For small coagulation plants, the solution is prepared in ordinary tanks (Fig. 8.9). The dry reagent is loaded into wire basket *1* through which the tank is filled with water *3*. The solution is stirred with the aid of air or steam suppled through bubbler *2*.
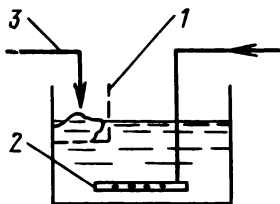
Fig. 8.9. Tank for dissolving chemicals

The method of preparing process solutions described above proves labour consuming and not suitable for high-output water-treating plants ($\geqslant 200$ t/h) where reagents are consumed in great quantities. The so-called "wet-storage" of reagents is then introduced. The reagents, in an amount sufficient for monthly or longer operation, are charged into a reinforced-concrete cell located at the floor level or below it.

In this way saturated solutions of reagents form in the cells. The solutions are diluted to required concentrations in pipelines, in ejectors or distributer tanks. When wet storage of reagents is

applied, measures must be taken to prevent filtration of the solution through the reinforced-concrete walls of the cell and also to preclude possible damage to the walls of the confining cell. The quantity of reagent fed to consumers is measured by means of a flowmeter or estimated by the drop in reagent level in the cell. If the commercial chemical contains impurities, the solution is to be permitted to settle and filtered prior to usage.

Coagulant solutions are acid and attack metal intensively. That is why, at small-output plants the solutions are prepared and kept in storage in wooden tanks. Metal apparatus (tanks, metering devices, pumps) must be provided with acid-resistant coatings or made from acid-resistant grades of steel. Reinforced-concrete cells must also have acid-resistant coatings.

8.5.4. Metering (Dosing) Solutions of Reagents

Solutions of reagents are introduced into water by means of devices or apparatus, known as metering devices. A metering device must accurately maintain and feed the preset amount of reagent within the entire load range of the water-treatment plant. As metering of a reagent takes place, the quality of the water treated must remain unchanged. Otherwise, the attending personnel must intervene to remedy the trouble, since many of the metering devices used are "insensitive" to changes in water quality. It follows that with respect to "quality", the amount of the reagent fed by a metering device is controlled by the personnel of a water-treatment plant, and with respect to "quantity" by the metering device itself. This operating principle of metering devices can be considered suitable since the quality of water changes gradually and only during individual seasons of the year.

Metering devices are available in a variety of designs. They must act automatically, i.e. must change the amount (dose) of the chemical introduced upon a change in the rate of water flow, Q. That is why the quantity Q is usually used to bring into action the actuating mechanism of a metering (proportioning) device. The pH value of a medium or its conductivity can also serve the same purpose in automated metering devices.

Plunger-type metering pumps are most commonly employed for dosing solutions of hydrazine, ammonia, phosphates, alkaline compounds of sodium, coagulants, and of other chemicals used in

water treatment. In metering devices of this kind the feed rate of reagents is varied by changing the plunger stroke or the number of plunger strokes, i.e. the speed of the electric motor driving the pump. The third way of changing the feed is to control the pump's operating time, with motor speed and plunger stroke kept constant. This pulse-type operation of metering devices is characterized by the ratio

$$\gamma = \frac{t_0}{t_0 + t_i} \tag{8.13}$$

where t_0 and t_i denote motor's operating time and idling time, respectively.

The values of t_0 and t_i are specified while setting up the equipment and maintained within the preset limits by a special electron controller which receives commands from the transducer of a flowmeter. For metering devices handling milk of lime the following operation and idling times are recommended: $t_0 \geqslant 10$ s and $t_i \leqslant 30$ s. Under sufficiently steady-state operating conditions, metering pumps can be operated without automatic control.
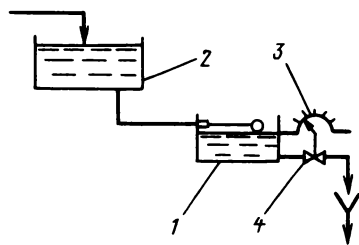
Fig. 8.10. Layout for metering dissolved reagent with plug valve

Small-capacity water-treatment units operated at industrial power plants or boiler houses can use other metering devices and employ other methods of dosing solutions of chemicals, the so-called open-type metering devices. The simplest metering device depicted schematically in Fig. 8.10 uses preliminarily calibrated plug valve 4. The reagent fed from tank 2 into tank 1 is maintained at a constant level. The divisions on scale 3 marked in the process of calibrating plug valve 4 indicate the reagent's rate of flow q, l/min. If the rate of water flow is sufficiently stable and the reagent solution is free of a precipitate, this metering device can perform adequately.

The layout of an automatically-controlled syphon-type metering device is illustrated in Fig. 8.11. The dissolved reagent is delivered from service tank *1* to tank *2*, in which a constant level of the solution is maintained by a float-type level controller. Wire rope *4* connects syphon pipe *3* to float *5*. The water being treated, *13*, flows to device *7* which separates from the main flow a small fraction of water, *15*, going into tank *6*. Water leaves the tank through hole *8*, whose clear passage can be varied by means of pulley(*10*)-controlled cone *9*, and passes into funnel *12* from which this fraction of flow is directed together with main flow *14*, for instance, into a tank or reactor. Under steady-state conditions, the same amount of water enters and leaves tank *6*. As load *13*
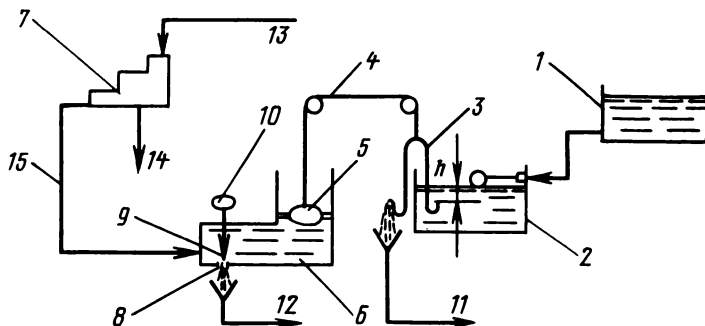
Fig. 8.11. Layout of siphon-type metering device

increases, the rate of water flow *15* increases too, so that the water level in tank *6* rises. The syphon pipe will sink deeper and the feed rate of reagent *11*, m³/s, will increase in proportion to *h*

$$V'_s = \mu f \sqrt{2gh}$$

where $\mu \approx 0.65$ = discharge coefficient
f = cross-sectional area of syphon pipe, m²
h = syphon-pipe submergence depth, m

The reverse is true when the load carried by the water-treatment plant diminishes, so that the rate of solution dosing is reduced.

Some demerits are associated with open-type metering devices. One of them consists in that the water-treatment equipment must be arranged at some height above the floor level since the metering

devices must be mounted on top of the tank that receives the solution, with the water distributer placed above them.

Of the pressure-type devices, in addition to metering pumps, use is made of orifice-type metering devices whose principle of operation is based on the pressure drop through an orifice (Fig. 8.12). If closed tank *2* filled with a solution is connected to an
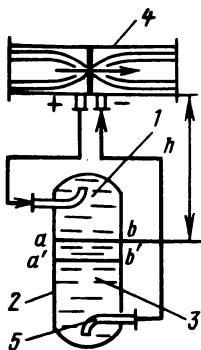
Fig. 8.12. Layout of orifice-type metering device

orifice, water will begin to flow into it and displace into pipeline *4* a certain amount of the solution. Between water layer *1* and solution layer *3* a transition layer forms, which is confined by planes *ab* and *a'b'*. The concentration of the reagent in this layer varies from zero (in plane *ab*) to the preset value. The presence of this layer is one of the shortcomings of orifice-type metering devices, since when plane *a'b'* coincides with the hole in pipe *5*, dosing accuracy becomes disturbed. The transition layer may be of considerable height if the solution temperature differs greatly from the water temperature.

The metering device shown schematically in Fig. 8.13 permits dosing of reagents into an open tank without the use of a water distributer. The impulse used for reagent metering is the pressure drop through throttling orifice *1* arranged in the water pipeline. This impulse is transformed by measuring instrument *2* into an electric signal fed to amplifier *3* which sends a command to actuating mechanism *5*. The latter incorporates a reversible motor fitted with profiled cam *6* that changes the degree of opening of needle valve *4* controlling the rate of reagent flow into the open tank.

A reagent can be fed into the pressure pipeline by means of
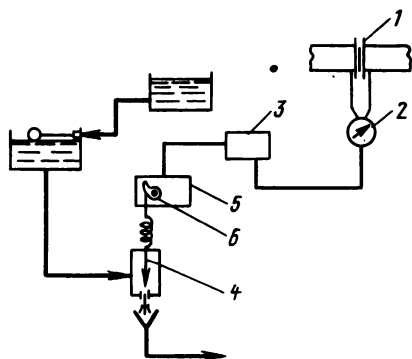
Fig. 8.13. Layout of metering device used for dosing easily soluble reagents into an open tank
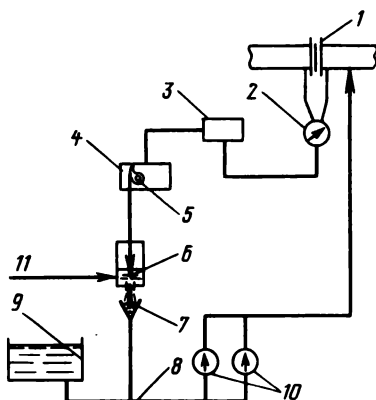
Fig. 8.14. Layout of metering device used for dosing easily soluble reagents into a pressure pipeline

a metering device depicted schematically in Fig. 8.14. It differs from the metering device illustrated in Fig. 8.13 in that it doses (measures) clarified water instead of a dissolved reagent. This precludes clogging of the valve by different impurities commonly present in dissolved chemicals and also corrosion of the valve (when using acid reagents). In this metering device, the impulse is transmitted from orifice *1* to actuating mechanism *4* via instrument

2 and electric-signal amplifier *3*. Profiled cam *5* varies the degree of opening of controlling valve *6* to which clarified water *11* is delivered from the tank where a constant level is maintained. The metered flow of water passes into funnel *7* and further into pipeline *8*, through which the reagent solution flows from tank *9* to plunger-type pumps *10* of the metering device. The pumps operate at a constant rate, so that the amount of solution remains constant and only the concentration of the solution varies.

8.5.5. *Layouts of Coagulation Plants*

Two basically different modes of coagulation are used: (a) coagulation in a clarifier or settling tank and (b) coagulation in clarifying filters. The layout fitted with settling tanks will be considered below. The layout of a coagulation plant with clarifying filters is shown in Fig. 8.15. Pump *1* delivers the water to be treated
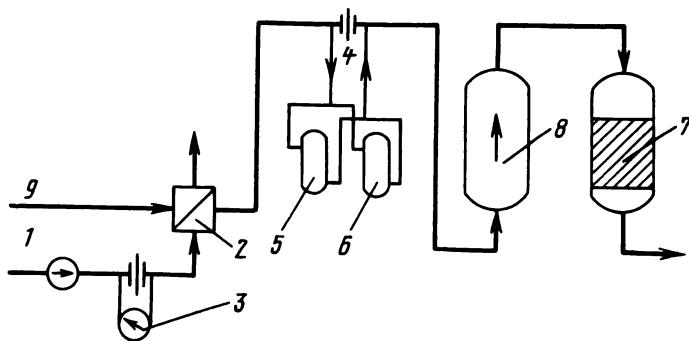
Fig. 8.15. Hookup of a direct-flow coagulation plant

into surface heat exchanger *2*, in which water is heated by steam *9* or hot water to 303-308 K. The amount of water is measured by flowmeter *3*. Orifice (or pump-type) metering devices *5* and *6*, respectively for an alkali and coagulant, are connected to throttling orifice *4*. The precipitates being formed are trapped in clarifying filters *7*. Sometimes (when difficultly coagulated waters are treated), mixer *8* is installed upstream of the clarifying filters. The mixer is a hollow cylindrical vessel in which water flows from below upwards with a velocity sufficient to preclude precipitation

and accumulation of residue in the mixer. The purpose of the mixer is to ensure better mixing of the reagents and water and to prolong coagulation.

8.6. Condensate Deferrization

8.6.1. Deferrization of Turbine Condensate in Bed-Type and Tubular-Element Precoat-Type Filters

Ferrous oxides, Fe_2O_3 and Fe_3O_4, are dispersed in condensate in the form of particles measuring 0.1 to 1.5 μm in size. They can be removed from turbine condensate by passing the latter through clarifying (mechanical) filters with beds built up of various materials: sulphonated carbon, crushed anthracite, cellulose, etc. The amount of oxides present in the turbine condensate of supercritical-pressure boiler-turbine units does not exceed 10 to 15 μg/kg when the units are in steady-state operation, but usually it lies within 6 to 10 μg/kg (corrected to Fe). At electric power stations fitted with natural-circulation boiler units operated at high- and supercritical pressures, the concentration of iron in turbine condensate reaches 30 to 100 μg/kg. When supercritical-pressure boiler units operate in unsteady conditions, the concentration of Fe in turbine condensate may increase to 200 to 300 μg/kg and more.

Condensate is treated (polished) in clarifying filters with a bed built up of sulphonated carbon and in tubular-element precoat-type filters with cellulose or ion-exchange materials. The filtering rates are 40 to 50 m/h in sulphonated-carbon filters (softeners) and 10 m/h in tubular-element precoat-type filters. But the latter have a considerably larger filtering surface (see Subsec. 8.2.3) and thus a greater throughput than the former (500 m³/h and 120 m³/h, respectively, with the diameter of filters being the same, 2 m). Sulphonated-carbon filters have found wide application at modern Soviet power stations equipped with high-power boiler-turbine units. Under normal operating conditions of a boiler-turbine unit, sulphonated-carbon filters are taken out of service every 3 or 4 months for washing or regeneration with acids. At some district power stations filters are operated without any regeneration and only washed 2 or 3 times per year. The experience gained at these power stations shows that rarely washed and nonregenerated sulphonated-carbon filters better retain iron oxide than systematically

washed or acid-regenerated filters. This is because a magnetite' film forms on the surface of the sulphonated-carbon bed long kept in service without washing. The film improves the trapping capacity of the filter.

Tubular-element precoat-type cellulose filters have a filtering run of 1 or 2 months, depending on the iron concentration in the condensate being treated. The degree of deferrization reaches 45 to 55 per cent both in sulphonated-carbon and cellulose filters. The latter show better performance, but require more intricate servicing. Operation of these filters is associated with the disposal of waste cellulose or ion-exchange powders, which hampers the treatment of waste waters. Filters of the two types keep the concentration of iron in turbine condensate to the prescribed standards ($\leqslant 10$ µg/kg).

8.6.2. Deferrization
of Industrial Condensates

The name industrial condensate is given to the condensate formed in the processing equipment of industrial enterprises, various-purpose heat exchangers, air heaters, steam jackets of reactors, condensers, etc. Industrial condensates are often returned to electric power stations, which supply enterprises with steam, or to boiler units operated in large industrial boiler houses. It is therefore essential that the returned condensate should contain a minimum amount of iron oxides, i.e. should comply with the requirements imposed on boiler units. However, practice shows that industrial condensate is usually heavily contaminated with iron whose concentration sometimes reaches 1000 to 1500 µg/kg and more. The main cause of such contamination is the corrosion of steam-condensate circuits. The presence of free carbon dioxide in steam, infiltration of oxygen (air in open return-condensate circuits), and high temperature of steam (353 to 373 K) create favourable conditions for intensive corrosion of equipment and pipelines.

Trying to get rid of iron impurities, enterprises which return industrial condensates to steam suppliers consider it advantageous to have deferrization facilities at their disposal. Meanwhile, a more correct way to persue is to eliminate the conditions that favour corrosion. Thus, the content of free CO_2 in condensate can be reduced to a minimum by rationally venting the steam spaces in heat exchangers or by treating the condensate in a decarburization plant. It is advisable to neutralize the remaining CO_2 with

ammonia if the use of this chemical is not prohibitive in the given conditions and to raise the pH value of condensate to 8.5-9.0. It is also expedient to accumulate returned condensate in a closed system operated at some pressure to prevent air infiltration into the system.

Experience shows that these undertakings often suffice to reduce the iron concentration in condensate down to 100 μg/kg. After taking the above measures, the problem of erecting a deferrization plant can be considered. Such a plant usually comprises conventional nonregenerated filters with sulphonated-carbon beds. Filters have to be regenerated if they are simultaneously used for softening of condensate. It is not advisable to employ filters with cellulose, perlite or ionite coatings for polishing industrial condensates due to operational difficulties (frequent regenerations, difficulties involved in the disposal of waste materials).

8.6.3. Condensate Deferrization by Means of Electromagnetic Filters

Electromagnetic filters have recently found application in removing from water and condensate iron oxides possessing ferromagnetic properties: magnetite, Fe_3O_4 (black), hematite, γ-Fe_2O_3 (brown), and also compounds (ferrites) such as $CuO \cdot Fe_2O_3$, $ZnO \cdot Fe_2O_3$ and others.

An electromagnetic filter (Fig. 8.16) consists of filter proper (casing) *1* enveloped by electromagnetic coil (solenoid) *3* and ferromagnetic-steel balls *6* loaded into the filter. The filter is supported by legs *7*. When direct current flows through the coil, a magnetic field is induced around the turns of the coil. The lines of force *4* of this field permeate the layer of balls, creating in the spaces between the balls a high magnetic field strength sufficient to retain fine iron-oxide particles. Outside the filter the magnetic lines of force pass far beyond the coil, encircle it and close in the layer of balls. This means that a magnetic field can be detected around the filter at a distance of 1.5 to 2.0 m and this fact should not be overlooked. The magnetic dispersion can be prevented by covering the coil with external magnetic circuits. Dispersion reduces materially the fraction of the effectively used electromotive force.

Some of the electric power consumed by the coil converts into heat that must be removed, i.e., the coil must be cooled reliably. When natural cooling of the coil is applied, the draft is increased by

providing jacket *2* around the filter. The circulation of the cooling air is indicated by arrows. The condensate to be treated goes into the filter through valve *8*, flows upward through the layer of balls with a velocity equal to 1000 m/h and leaves the filter through valve *10*. Upon exhaustion of the iron capacity of the balls, equal to 1.5-2.0 g/kg of balls, the filter is taken out of service for washing.
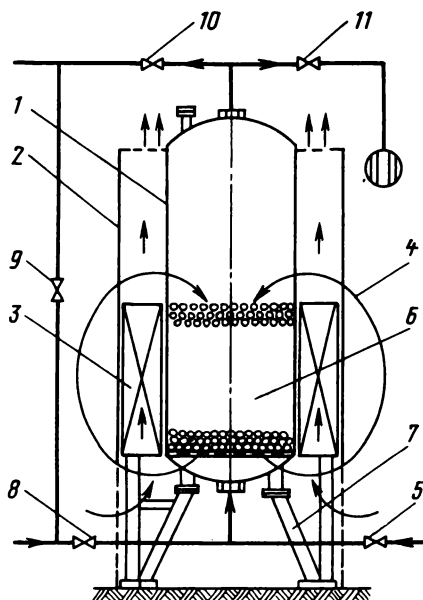
Fig. 8.16. Schematic of an electromagnetic filter

For this purpose valve *9* is opened on the by-pass line, valves *10* and *8* are closed, the coil is deenergized to allow the balls to demagnetize. Then, valves *5* and *11* are opened and the filter is washed for 1 min. All these operations are performed automatically following the prescribed program. After washing is terminated, the filter is put into operation and connected to the condensate main.

At district electric power stations operating supercritical-pressure boiler units, the degree of deferrization in electromagnetic filters does not exceed 45 to 55 per cent; at an initial iron concentration of 8 to 10 µg/kg, the iron concentration in the filtrate amounts to 4 or 5 µg/kg and less. Since filters of this kind are heatproof, they

may be installed anywhere in the flow circuit of a boiler-turbine unit.

One of the main characteristics of an electromagnetic filter is the magnetic field strength H, A/m, calculated by the formula

$$H = \frac{18\mu_w v_p \cdot 10}{\mu_0 \rho_p \operatorname{grad} H d_p^2 \chi}$$ (8.14)

where μ_w = water viscosity, kg s/m^2
$\quad\quad d_p$ = diameter of iron oxide particle, m
$\quad\quad v_p$ = particle velocity, m/s
$\quad\quad \mu_0$ = permeability of free space, H/m
$\quad\quad \chi$ = magnetic susceptibility of particle, m^3/kg
$\operatorname{grad} H$ = gradient of magnetic field strength in interball space, A/m^2
$\quad\quad \rho_p$ = particle density, kg/m^3

All quantities, apart from v_p and d_p, are constant for a given electromagnetic filter. Formula (8.14) can thus be written as

$$H = K\frac{v_p}{d_p^2}$$ (8.15)

where $K = 18\,\mu_w \cdot 10/\mu_0 \rho_p \operatorname{grad} H\chi$

It follows that the removal of fine magnetite particles requires a magnetic field of high strength, i.e. high-power electromagnetic coils.

8.7. Oil Removal from Condensate

The condensate returned from industrial steam consumers to electric power stations often contains oil (petroleum products). Some steam consumers contaminate condensate with oil continuously and others periodically. The former consumers are various-purpose reciprocating steam engines, and the latter are most of the steam consumers at by-product coke enterprises, petroleum refineries, where steam is used to heat petroleum products in surface-type heat exchangers. Steam consumers of the first group contaminate steam, so that the condensate becomes oil-contaminated. The content of oil in steam is comparatively low, about 150 to 200 mg/l, and is about constant for steam engines of

this type. The presence of oil in steam is responsible for the formation of stable oil emulsions in condensate.

The condensate returned from consumers of the second group is contaminated with oil in another manner. Here, oil gets into the condensate only, mostly when faulty heat-exchange equipment is operated, which permits oil leakage into the intertubular space filled with condensate. With sound heat-exchange equipment operated under normal conditions, condensate contains no oil or rather small amounts of oil.

For the first group of steam consumers, it is advisable to start with removing oil from the steam. This is done in mechanical oil-steam separators whose principle of operation reduces to the following: with abrupt changes in the direction of steam flow or its circular path, oil droplets are thrown out of the steam flow and adhere to the walls as the steam strikes them. In oil-steam separators steam follows an intricate path as it changes the direction of flow repeatedly and reflects from surfaces placed along its flow. Oil-steam separators reduce oil concentration in steam to 10-15 mg/l. Better removal of oil from steam is attained in steam washers in which the steam is forced to bubble through a layer of water. Here the residual oil concentration comes to 3-5 mg/l.

Oil is removed from condensate in a special deoiling plant (Fig. 8-17). Oil-contaminated condensate *1* passes into settling tank
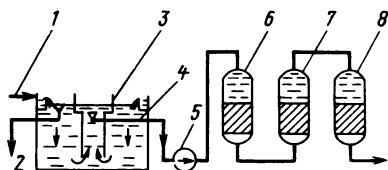
Fig. 8.17. Schematic of an oil removing plant

4, in which oil droplets separate from water during its upward flow in the tank. The oil accumulated on the surface is removed from the settling tank into collector *2*. Pump *5* draws condensate from the upper part of central tube *3* and delivers it to clarifying filters *6*, whose beds consist of crushed coke or anthracite of 1-2 mm piece size. These filters remove droplets of oil contained in the condensate. Then the condensate is passed through sorption filters *7* loaded with activated carbon, where the concentration of oil in the condensate is reduced to 0.5-1.0 mg/kg.

After treatment in clarifying and sorption filters, the hardness of condensate grows markedly due to an increased content of silica compounds and salts. That is why the condensate is often treated additionally in cation-exchange softeners *8* downstream from the sorption filters. But if the condensate is destined for high-pressure boiler units, it must be treated in demineralizing and silica removal facilities of water-treatment plants. The increase in condensate hardness and its contamination with other impurities after the clarifying and sorption filters is due to the dissolution of ash impurities contained in the coke and activated carbon. The rate of condensate filtration is about 5 to 7 m/h. Oil may also be removed from condensate in tubular-element precoat-type filters using a mixture of powdered perlite and activated carbon as a filtering material.

Review Questions

1. What determines the rate of water filtration in mechanical filters?
2. Name the main characteristics of granular filtering beds used in a mechanical filter.
3. Describe the way of determining the optimal dose of a coagulant used for treatment of given water.
4. When are coagulants used?
5. Name the main conditions to be observed to ensure reliable and rapid water coagulation, $Al_2(SO_4)_3$, during the spring flood.
6. Describe the mechanism of removing ferrous compounds from condensate in an electromagnetic filter.

Chapter 9

Water Treatment by Precipitation of Scale-Making Materials

9.1. Softening Processes and Consumption of Reagent

9.1.1. Precipitation Methods

Water softening by precipitation of scale-making materials is based on binding calcium cations, Ca^{2+}, and magnesium cations, Mg^{2+}, with ions, CO_3^{2-} and OH^-; the chemical reaction results in the formation of difficultly soluble compounds, $CaCO_3$ and $Mg(OH)_2$, that precipitate out and are removed from the water. The CO_3^{2-} and OH^- ions are added to the water being treated with various reagents-precipitators such as caustic lime, CaO, or slaked lime, $Ca(OH)_2$, sodium hydrate (caustic soda), NaOH, and sodium carbonate (soda ash), Na_2CO_3. Depending on whether these reagents are used individually or in combinations, the following water-treatment methods are distinguished: lime treatment (or liming), soda-lime treatment, sodium hydrate treatment, soda-sodium hydrate treatment, lime-sodium hydrate treatment.

9.1.2. Lime Treatment

Liming is practiced where it is necessary to decrease the alkalinity of initial water. This method does not result in sufficiently deep water softening. The processes that develop during lime treatment of water can be represented by the following formulae in ionic form:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$
$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \qquad (9.1)$$
$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$
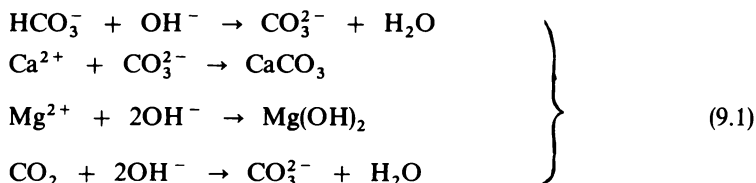
A study of these reactions shows that lime treatment affects the carbonate hardness (alkalinity) in the initial water; carbonate hardness decreases to 0.7-1.0 mg-equiv/l; magnesium is removed from water if there is a sufficient excess of OH⁻; the water-dissolved carbon dioxide is removed from water; the content of total solids in the lime-treated water diminishes; the total hardness in lime-treated water also decreases and becomes equal to

$$H_{lt} = H_{nc} + A_{lt} \tag{9.2}$$

The residual alkalinity of lime-treated water is

$$A_{lt} = (0.7\text{-}1.0) + \alpha \tag{9.3}$$

where α denotes the excessive amount of $Ca(OH)_2$ equal to 0.2 or 0.3 mg-equiv/l.

The alkalinity of water (for which $H_t \leqslant A_t$) can be reduced by adding to the water neutral calcium salts, for instance, $CaCl_2$, together with lime (where only lime treatment of water is applied). Then

$$\left. \begin{array}{l} 2NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + NaCO_3 + 2H_2O \\ Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl \end{array} \right\} \tag{9.4}$$
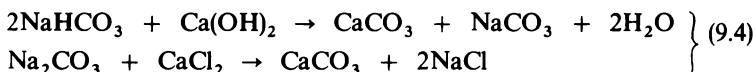
This method of water treatment, however, involves some increase of the total solids in water.

The content of total solids in lime-treated water is reduced due to removal of $CaCO_3$ and $MgCO_3$, which are the components of the total solids in the initial water, and also due to partial removal of various colloidal substances. A knowledge of the magnitude of the total solids, mg/kg, in the lime-treated water is essential in a number of cases. Where high accuracy is of no importance, the approximate value of the total solids can be calculated by formulae in which the terms are usually known from shortened water analysis:

$$\left. \begin{array}{l} S_{lt} = S_{iw} - 50(H_c - A_c^{lt}) + 8H_{Mg} + 37\alpha - 3.5\delta O \\[2mm] S_{lt} = S_{iw} - 50(H_{Ca} - A_c^{lt}) - 42(H_c - H_{Ca}) \\[1mm] \qquad + 8H_{nc} + 37\alpha - 3.5\delta O \end{array} \right\} \tag{9.5}$$

where S_{iw} = total solids in initial water, mg/kg
$\qquad A_c^{lt}$ = carbonate alkalinity of lime-treated water, mg-equiv/kg
$\qquad O$ = oxidizability

The first formula is applicable to natural nonalkaline waters, for which the ratio $C_{Ca^{2+}}/C_{(HCO_3^-)} \geqslant 1$, and the second to waters with a ratio $C_{Ca^{2+}}/C_{HCO_3^-} < 1$. The accuracy of these formulae usually falls within 5 to 10 per cent.

In treating waters of the first group, for which $H_t > A_t$, the consumption of 100 per cent lime, g_l, mg/kg, is calculated by the formula

$$g_l = 28(H_c + H_{Mg} + H_{CO_2} + C + \alpha) = 28R_l \qquad (9.6)$$

where R_l = dose of lime introduced, mg-equiv/kg
    C = dose of coagulant introduced, mg-equiv/kg

The amount of commercial lime required for treatment, g_l, mg/kg, can be calculated by the following formulae:

$$g_l = 2800R_l/C_l \qquad (9.7)$$

or

$$g_l' = 2.8Q_gR_l/C_l \qquad (9.7a)$$

where C_l denotes the content of CaO in the commercial chemical, which should not be less than 60 per cent.

Formula (9.6) also accounts for the consumption of lime spent on precipitation of magnesium, whose removal is not at all obligatory in a number of cases. Moreover, it calls for an added consumption of lime and sometimes deteriorates the operation of clarifying facilities. So, complete precipitation of magnesium must be avoided whenever possible. For waters with a ratio $C_{Ca^{2+}}/C_{HCO_3^-} \geqslant 1$, magnesium cannot be precipitated at all. The dose of lime for the case in hand is calculated by the formula

$$R_l = H_c + H_{CO_2} + C + \alpha \qquad (9.8)$$

Lime treatment of water is controlled by the concentration of calcium in the lime-treated water, $C_{(Ca^{2+})}$, which should be about equal to A_{iw}, where A_{iw} denotes the alkalinity of initial water, and $C_{Ca^{2+}}$ the concentration of Ca in initial water.

But when $C_{Ca^{2+}}/C_{HCO_3^-} < 1$, magnesium must inevitably be precipitated in the amount of $A_{iw} - H_{Ca}$, and the quantity of lime is then

$$R_l'' = H_c + H_{CO_2} + (A_{iw} - H_{Ca}) + C + \alpha \qquad (9.9)$$

Lime treatment of water is then controlled by the concentration of magnesium in the lime-treated water, which approximately equals $H_t - A_{iw}$. The liming process where the consumption of lime is calculated by formula (9.8) or (9.9) is called *carbonate*. This name is conditional since the water contains some excessive amount of hydrates.

9.1.3. Water Treatment with Soda and Lime

In distinction to liming, this method permits water softening to 300-400 µg-equiv/kg. When heated to high temperatures, some waters can be softened to a residual hardness of about 200 µg-equiv/kg. Lime decreases H_c, H_{Mg} and removes CO_2 from the water. Noncarbonate hardness that shows up after liming due mainly to calcium compounds is got rid of by soda ash:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{9.10}$$
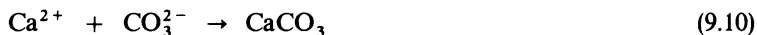
The consumption of soda, mg/kg, is determined by the formula

$$g = 53(H_{nc} + C + \beta) \tag{9.11}$$

or, kg/h,

$$g' = \frac{5.3Q_g(H_{nc} + C + \beta)}{C} \tag{9.12}$$

where $\beta = 1.0\text{-}1.5$ = excess amount of soda over the stoichiometric quantity, mg-equiv/kg
$C = Na_2CO_3$ content in commercial product, per cent

When it is treated with soda and lime, water is heated to 363-368 K. This kind of water treatment is inapplicable to alkaline waters.

9.1.4. Water Treatment with Sodium Hydrate and Soda

The interaction of NaOH with calcium and magnesium compounds proceeds according to reactions similar to reactions (9.1). The process of water treatment with sodium hydrate is characterized by the formation of soda ash, or washing soda, due to the interaction

of NaOH with calcium bicarbonate and magnesium bicarbonate. The amount of Na_2CO_3 that forms in the reaction, mg-equiv/l, will be equal to $2H_c$. If the excess of ions, CO_3^{2-}, mg-equiv/l, in the softened water is β, then water softening by sodium hydrate alone becomes expedient on condition that the equality

$$2H_c + H_{CO_2} = H_{Ca} + \beta \tag{9.13}$$

is valid for the natural water.

The left-hand side of Eq. (9.13) determines the amount of ions, CO_3^{2-}, being formed, and the right-hand side characterizes the quantity of these ions required for the given water. If $2H_c + H_{CO_2} > H_{Ca} + \beta$, CaO is to be added to the water being treated to bind the excess ions, CO_3^{2-}, in which case the water is treated due to the combination of reagents, CaO + NaOH. When $2H_c + H_{CO_2} < H_{Ca} + \beta$, the shortage in ions, CO_3^{2-}, is compensated for by introducing washing soda into the water to carry out the treatment with a combination of reagents, NaOH + Na_2CO_3. The consumption of the chemicals can be calculated by the formulae:

Treatment method	Reagent consumption, g/m^3	
With sodium hydrate	$(NaOH) = 40(H_c + H_{Mg} + H_{CO_2} + C + \alpha)$	
With soda and sodium hydrate	$(NaOH) = 40(H_c + H_{Mg} + H_{CO_2} + C + \alpha)$	
	$(Na_2CO_3) = 53(H_{Ca} - 2H_c + H_{CO_2} + \beta)$	(9.13a)
With lime and sodium hydrate	$(CaO) = 28(2H_c + H_{CO_2} - H_{Ca} + \beta)$	
	$(NaOH) = 40(H_{nc} + C + \alpha + \beta)$	

9.2.   Clarifiers

Figure 9.1 illustrates schematically a Soviet-made clarifier used for lime treatment. The water being treated, *1*, is heated to the preset temperature and delivered to distributing system *8*, which is located in air separator *14* to free the water from air bubbles. The water then flows downward in tube *10* to tangentially-arranged inlet *21* and passes into mixer *20*. The required chemicals such as lime *2*, coagulant *3*, and flocculant (polyacrylamide) *4* are also fed into the mixer via radially-arranged inlets. Such arrangement of the inlets (one over the other) contributes to better formation and separation of the precipitate. The dissolved coagulant can also be introduced into the pipeline *24* for the water being treated.
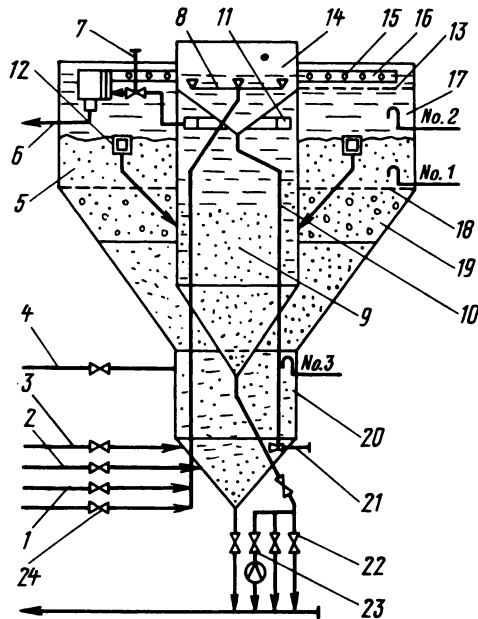
Fig. 9.1. Vertical-flow sludge-blanket clarifier for lime treatment of water

All the reactions involved in liming and coagulation proceed in the mixer and result in precipitation of impurities from the water. The water flows upward from the mixer, so that the particles consolidate, flocs form and accumulate in some volume, forming sludge blanket zone *5*, which is of great importance to clarifier efficiency.

The top level of the sludge blanket zone is almost at the level of sludge discharge ports *12*. The surplus sludge is discharged through these ports into sludge concentrator *9* where the precipitate settles, consolidates and accumulates in the bottom part of the concentrator. The residue in the form of a concentrated sludge is drained off continuously from the concentrator through valve *22* or *23*. The clarified water moves upward in the sludge concentrator and goes to collecting trough *16* and further into circuit *6* via water intake *11* and valve *7*.

From 15 to 20 per cent of the entire volume of water can be

diverted into the sludge concentrator. As it leaves the sludge blanket, the remaining part of the water becomes completely free of the suspended matter in clarifying zone *17*, passes to water collecting trough *16* and flows from the clarifier through openings *15*. Perforated grid *19* serves to quench the rotational motion of water, grids *18* and *13* distribute the water over the entire cross-sectional area of the clarifier.

9.3. Attendance of Clarifiers

Attendance of clarifiers consists in practicing operational control of clarifier performance so as to produce clarified (lime-treated) water of preset quality. This objective is accomplished proceeding from the knowledge of the following regularities associated with the operation of a clarifier.

The balance equation for the impurities deposited in a clarifier has the form

$$Q_{iw}C_{iw} = q_{sb}C_{sb} + R \tag{9.14}$$

where Q_{iw} = quantity of water treated in clarifier, m^3/h
q_{sb} = quantity of sludge discharged from the sludge concentrator (blowdown of the clarifier), m^3/h
C_{iw}, C_{sb} = concentration of precipitated substances in the initial and blowdown water respectively, mg/l
R = amount of sludge removed directly from the clarifier, g/h

The concentration of precipitate in the initial water is

$$C_{iw} = 100\,(A_{iw} - A_{tr}) + 29\,(H_{Mg} + H'_{Mg}) + d_c E_c + C_i \tag{9.15}$$

where A_{iw}, A_{tr} = carbonate alkalinity of the initial and treated water respectively, mg-equiv/kg
H_{Mg}, H'_{Mg} = magnesium hardness of the initial and treated water respectively, mg-equiv/kg
d_c = dose of coagulant, mg-equiv/kg
E_c = equivalent mass of coagulant hydroxide, mg/mg-equiv
C_i = concentration of suspended substance in water upstream of clarifier

The value of C_{iw} can be determined by trial softening of the

initial water. If coagulation is absent, $d_c E_c = 0$ in Eq. (9.15).

It is most expedient that a clarifier could operate at $R = 0$. To meet this condition, it is necessary that

$$Q_{iw}C_{iw} = q_{sc}C_{sc} \tag{9.16}$$

or

$$q_{sc} = C_{iw}Q_{iw}/C_{sc} \tag{9.17}$$

where q_{s_t} = quantity of sludge passing into sludge concentrator, m³/h

C_{sc} = solid phase concentration in the sludge (blanket), mg/kg

The quantity of clarified water leaving the sludge concentrator, referred to as "cutoff", can be calculated by the formula

$$q_c = q_{sc} - q_{sb}$$

The amount of sludge passing into the sludge concentrator and, consequently, the cutoff q_c depend on C_{sc} (for a given quality of initial water). In general, q_c amounts to 5 to 10 per cent of Q_{iw}. It is however desirable that the clarifier's design should permit, whenever necessary, increasing the amount of cutoff to 15 to 20 per cent, thereby enabling a better control of the apparatus. If the concentration of suspended substances in the clarified water leaving the sludge concentrator amounts to C_c, mg/kg, then the cutoff can be increased so far as the condition

$$C_c \leqslant Q_{iw}C_{cw}/q_{sc} \tag{9.18}$$

is observed (C_{cw} denotes the admissible concentration of suspended substances in the water leaving a clarifier, mg/kg).

Small values of q_c ($\leqslant 5$ per cent) indicate that the pressure drop in the system for diverting water from the sludge concentrator is rather great and must be decreased. If q_c cannot be increased, then the difference $q_{sc} - q_c = q_{sb}$, m³/h, is removed from the clarifier through the sludge concentrator, though this involves water and reagent losses.

The amount of sludge removed by continuous blowdown from the sludge concentrator, q'_{sb} per cent, is calculated by the formulae

$$q'_{sb} = \frac{q_{sb}}{Q_{iw}}100 = \frac{C_{iw}}{C_{sb}}100 = \frac{C_{sc}}{C_{sb}}\frac{q_{sc}}{Q_{iw}}100 \tag{9.19}$$

As seen from Eq. (9.19), one can decrease q'_{sb} by increasing C_{sb}

and C_{sc}, i.e. the solid phase concentration in the clarifier's sludge blanket zone and in the sludge concentrator. It is advisable to keep C_{sc} equal to 1-1.5 and C_{sb} to 10-15 g/kg. In liming, C_{sc} is usually increased using a coagulant and a flocculator. To improve performance of a clarifier and produce sufficiently clarified water from low-turbidity initial water subject to coagulation only, it is expedient to increase its turbidity by adding, for example, clay in an amount of about 10 to 30 mg/kg or somewhat more. This ensures the formation of a heavy sludge blanket with $C_{sc} = 0.5$ to 1.0 per cent and results in better clarification of coagulated water and proper control of the process.

A clarifier is controlled by analysing water samples taken from its various spots. Among the many water sampling points, three are most important. These are point *1* (see Fig. 9.1) located 0.5 to 0.6 m below the normal level of the suspended precipitate, point *2* arranged 1.0 to 1.2 m above the first, and point *3* in the lower part of the mixer. For a clarifier operated under normal conditions, the sludge blanket level must lie between points *1* and *2*. The precipitate found in the water sample taken at point *2* is indicative of improper operation of the clarifier. The level of the sludge blanket must then be lowered by blowing down intensively the sludge concentrator. A clarifier is put into operation under a load equal to 50-60 per cent of the rated value. The load can be gradually increased as the amount of sludge in the blanket zone reaches 0.2 to 0.3 per cent.

9.4.   Preparing and Dosing Milk of Lime

The milk of lime is a suspension of solid nondissolved particles of lime, $Ca(OH)_2$, in the saturated lime solution. In small-capacity clarifying plants the milk of lime is prepared in mixers illustrated in Fig. 9.2. Unslaked lime, CaO, is charged into a tank, poured over with water and left to stand 2 to 4 hours for its slaking by the reaction

$$CaO + H_2O =_{\backslash} Ca(OH)_2$$
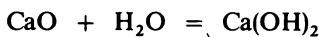
This reaction proceeds with heat evolution (approximately 1170 J/kg), so that the entire mass of lime heats up and water evaporates. This calls for isolating the slaking facilities from other rooms or fitting them with exhaust ventilation means. After slaking, the formed dough is thinned with water and drained off into
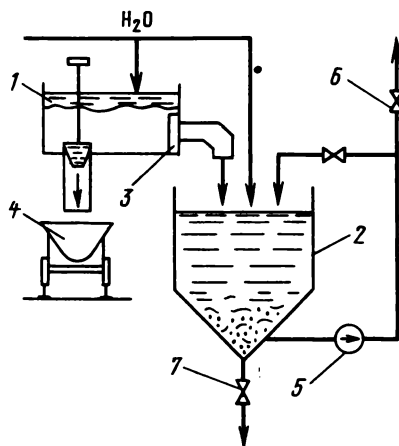
Fig. 9.2. Preparation of milk of lime in a mixer

1 — slaking tank; *2* — mixer; *3* — strainer; *4* — car; *5* — circulation pump; *6* — to feeder or saturator; *7* — drain
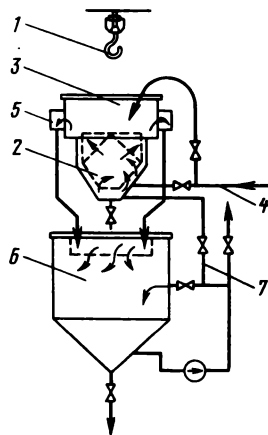
Fig. 9.3. Milk-of-lime preparation unit

a mixer. The nondissolved admixtures and other impurities remaining in the slaking tank are disposed of as waste. The thick milk of lime drained into the mixer is diluted with water, mixed by circulation with the aid of a pump and delivered to a metering device (feeder).

A more advanced layout for preparing milk of lime is depicted in Fig. 9.3. Lime is delivered from the storage by electric hoist *1* in special wire baskets *2* that are placed in slaking tank *3*. Then the tank is closed hermetically and filled with water, which is delivered under pressure through tube *4*. The ascending water slakes and washes out the lime, then flows over pockets *5* into mixer *6*. To speed up the slaking process, the lime is also washed out by means of a circulation pump through branch pipe *7*. The basket is then hoisted from the tank and the inert constituents left in it are discharged into a dump. The empty basket is again filled with lime.
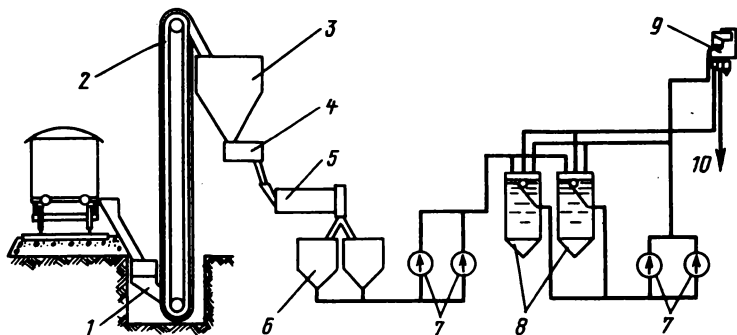
Fig. 9.4. Mechanized unit for preparation of milk of lime

1 — crusher; *2* — elevator; *3* — hopper; *4* — feeder; *5* — slaking drum; *6* — tanks for milk of lime; *7* — pumps; *8* — mixing tanks; *9* — milk-of-lime metering device (feeder); *10* — to clarifier

But this layout cannot meet the requirements of high-capacity lime-treatment plants. Its main drawback is that the baskets are filled with lime by hand. This drawback is eliminated in the layout shown in Fig. 9.4, where all processes are mechanized. Lime can be delivered in cars, crushed and then charged by a bucket elevator into a receiving hopper, from which it is released into a rotating slaking drum. The ready milk of lime is collected in tanks of

sufficient capacity. The working concentration of milk is prepared in mixing tanks.   •

In the layout depicted in Fig. 9.5, lime is delivered to the water-treatment plant by motor transport in special containers loaded at the lime-producing plant or storage. The containers are handled by an electric hoist. Lime is slaked and washed out in the same manner as shown in Fig. 9.3. A great advantage of this layout
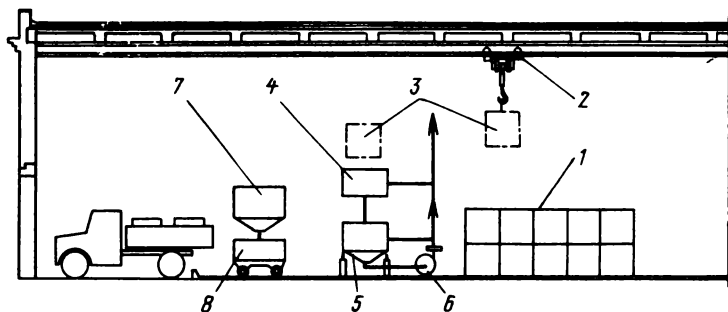
Fig. 9.5. Milk-of-lime preparation unit. Lime is delivered in containers

I — lime containers storehouse; *2* — electric hoist; *3* — container with lime; *4* — slaking tank; *5* — mixing tanks; *6* — pump; *7* — hopper; *8* — car for waste removal

is that it almost totally precludes the formation of lime dust. Nevertheless, these and other available layouts cannot be consider-ed suitable from the viewpoint of modern mechanization and automation of technological processes. The use of commercially produced powdery slaked lime is a decisive factor in tackling the problem.

Milk of lime is dosed by various metering devices (feeders). Plun-ger-type metering pumps have found wide application in up-to-date water-treatment plants. They allow for definite control of the amount of liquid by varying the plunger stroke or motor speed (rpm). The preset rate of feeding is provided by keeping the hy-draulic conditions at the pump's suction line invariable.

Figure 9.6 shows hookups used for dosing milk of lime by metering pumps. The concentration can be brought up to the required level in mixing tanks fitted with stirrers (Fig. 9.6a) or circulation pumps (Fig. 9.6b). Proper selection of equipment makes these hookups suitable for exact and dependable dosing of the

reagent. Preference should be given, however, to the hookup presented in Fig. 9.6a. All the layouts incorporate two mixers to permit continuous dosing and feeding of the reagent (one to be kept in service, the other filled with the reagent). The capacity of a mixer must ensure continuous operation of a water-treatment plant for 12 hours and longer.
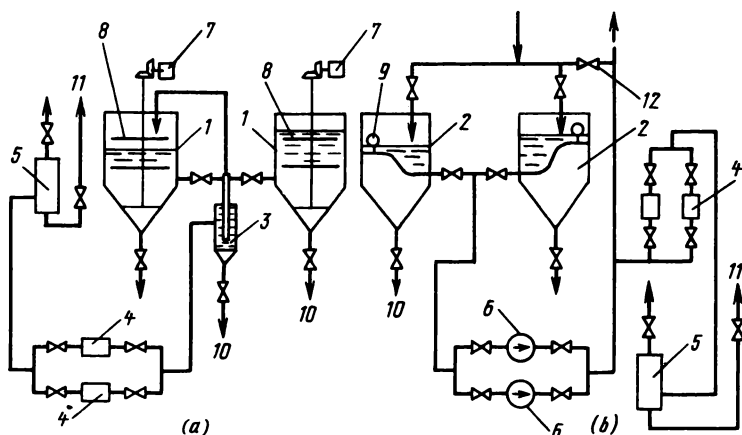
Fig. 9.6. Metering units of a lime-treatment plant

(a) mechanical mixing; (b) hydraulic mixing; 1 — mechanical mixer; 2 — mixing tank; 3 — sand trap; 4 — metering pump; 5 — air box; 6 — circulation pumps; 7 — electric drive of paddle mixer; 8 — mixer paddles; 9 — float; 10 — sludge drain; 11 — to clarifiers; 12 — return of excess milk of lime

At modern water-treatment plants, one strives to automatize the dosing of lime and other reagents so as to raise the dosing accuracy and simplify attendance of the plant. One of the possible automatic control systems is shown in Fig. 9.7. Sampled lime-treated water 1 passes through conductimetric pickup 2 that sends the signals representative of the conductivity of the water to regulator 7. The latter gives a command to actuating mechanism 8 to put into operation feeder 9 that measures off the requisite amount of milk of lime 10 and delivers it to the clarifier. Ejector 3, which receives treated water 4, ensures continuous flow of sampled water through pickup 2 into the clarifier, the initial dose being set up by set-point adjuster 6. When the quality of initial water changes, the rate of feed-

ing is corrected by regulator 7 as it receives the pulse from pickup 5 controlling the conductivity of samples of the water under treatment. Other automatic control systems are also available, but the main purpose they are assigned to serve remains the same as given above.
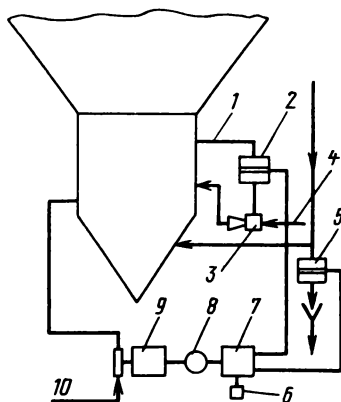
Fig. 9.7. Automatic feeding of milk of lime by means of metering pumps

9.5. Layout of Lime-Treatment Units

Lime-treatment units are installed upstream from water-treatment plants. They prepare water for the subsequent basic treatment practiced in water technology (softening, demineralizing). The layout of such a lime-treatment unit is shown in Fig. 9.8.

Initial water *14* is heated in heat exchanger *13* to 303-313 K and directed to clarifier *1*, to which are also delivered required reagents such as lime *11*, coagulant *10*, and flocculant *9* (polyacrylamide). The three reagents need not be used at a time; an expedient combination of them is determined in each particular case by trial treatment of the initial water. Lime-treated water *3* flows to intermediate tank *2*, from which pumps *6* draw the water and deliver it to clarifying filters *4* and further to ion-exchange equipment *5* of the water-treatment plant. Water is usually heated with steam *15*, and heater condensate *12* is directed to condensate tanks. The residue formed is removed from the clarifier through drain pipelines *7* and *8*.
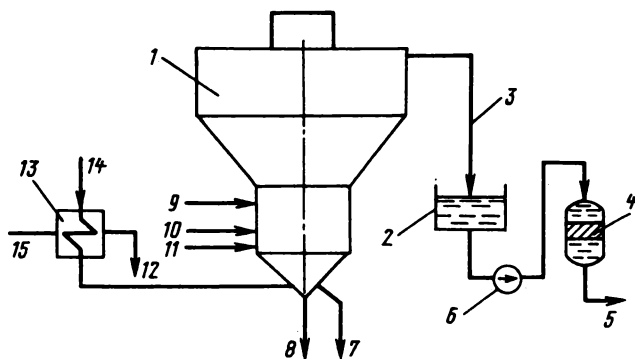
Fig. 9.8. Lime-pretreatment unit

9.6. Attendance of Lime-Treatment Units

Water leaving a clarifier must be transparent and stable. Stable water is the lime-treated water from which no hard deposits settle out as it flows along pipelines. If this is the case, operation of a lime-treatment unit may be considered adequate. The transparency of lime-treated water, as determined by the type method, must be not less than 30 cm. The quantity of suspended solids in the water must not exceed 20 mg/kg. The factors that make it impossible to obtain these parameters are inclined water-drain troughs, clogging of holes in the water-distributing system, excessive sludge deposits in the ports of sludge-receiving tubes, etc. These and other similar shortcomings disturb uniform water distribution over the entire cross-sectional area and volume of the clarifier. This results in the appearance of local high-velocity streams contributing to the carry-over of suspended solids. Clarifier performance is affected in the same manner when the rate of initial water flow through the clarifier changes abruptly and the water being treated is heated to different temperatures. Automatic control of a lime-treatment unit clears away abrupt variations in temperature and loading. An intense carry-over of suspended matter (especially in the event of water coagulation) may be observed when the concentration of precipitate in the sludge blanket zone is rather small ($\leqslant 0.1\%$). An increase in this parameter to 0.2 or 0.3 per cent remedies the situation.

The stability of lime-treated water is estimated by the stability

indicator

$$\Delta A = A_{tc} - A_{tf} \leqslant 0.15 \text{ mg-equiv/kg},$$

where A_{tc}, A_{tf} denote the total alkalinity of the filtered-water sample taken downstream of the clarifier and the clarifying filters respectively.

Heating the water under treatment to 303-313 K reduces ΔA. The presence of a sludge blanket in a clarifier and uniform distribution of the water over its entire cross-sectional area produce a similar effect.

Review Questions

1. Explain the design and operation of a clarifier.
2. Name the main characteristics that determine normal operation of a clarifier.
3. Making use of reactions (9.1), determine in a general way the theoretical dose of lime required for water treatment.
4. Describe the quality of initial water that permits lime treatment without precipitation of $Mg(OH)_2$. What are the advantages and disadvantages of operating a clarifier in such a manner?
5. Why is lime slaking accompanied by intensive evaporation of water?

Chapter 10

Water Treatment
by Cation-Exchange Processes

10.1. Essence
of the Cation-Exchange Process

The cation-exchange process is the exchange of cations of substances (electrolytes) dissolved in water with cations of a solid insoluble substance, called a cationite or cation exchanger, placed in this water.

The cation given up by a cationite to the solution in place of captured cations is called an *exchange cation*. Cation-exchange materials used in practice can contain various exchange cations. In water-treatment practice, however, three cations are of importance, namely, sodium, hydrogen, and ammonium cations. Depending on which of these cations a cation-exchange material is "charged" with, three cation-exchange processes are distinguished: the sodium cation-exchange process, the hydrogen cation-exchange process, and the ammonium cation-exchange process.

10.1.1. Sodium Cation-Exchange Process

The exchange cation here is sodium. When hard water is passed through the bed of sodium cationite, sodium cations are replaced by calcium and magnesium cations. The exchange reactions proceed as follows:

$$\left. \begin{array}{l} Ca^{2+} \ + \ 2Na^+R^- \ \rightarrow \ Ca^{2+}R_2^- \ + \ 2Na^+ \\[6pt] Mg^{2+} \ + \ 2Na^+R^- \ \rightarrow \ Mg^{2+}R_2^- \ + \ 2Na^+ \end{array} \right\} \qquad (10.1)$$
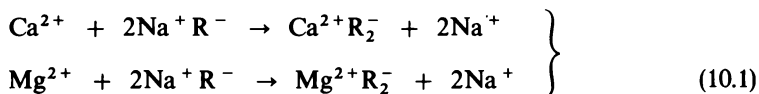
where the symbol Na^+R^- denotes the sodium cationite and R^- is the complex radical of the water-insoluble cationite that plays the part of a multivalent anion.

It follows from reactions (10.1) that in the sodium cation-ex-

change process only the cation composition of the water changes. The anions, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, and others present in the initial water pass into the treated (softened) water. Consequently, the alkalinity of the water treated does not decrease, which is a demerit of sodium cation-exchange water softening. What takes place here is only a more or less complete replacement of cations, Ca^{2+} and Mg^{2+}, by sodium cations. The result is that the hardness in water treated with sodium cationite drops to 10-15 µg-equiv/kg and less, and the content of total solids increases somewhat.

After all exchange cations of sodium are replaced by calcium and magnesium cations, the cation-exchange material is exhausted, i.e. becomes incapable of softening water. In this connection, a fresh cationite can be said to posses a certain capacity for absorbing cations, known as *operating exchange capacity e*. It is measured in gram-equivalents of cations absorbed by 1 m³ of the cationite, i.e. in g-equiv/m³. Thus, a cation exchanger becomes incapable of water softening after exhaustion of *e*.

To restore the operating exchange capacity of a cationite, the cations captured by the cationite must be removed and replaced by exchange sodium cations. This process is known as *regeneration* (restoration) of the cationite exchange capacity. It is accomplished by passing a NaCl solution through the bed of exhausted cationite. The regeneration reactions proceed in the following manner:

$$CaR_2 + 2n_sNaCl \rightarrow 2NaR + CaCl_2 + 2(n_s - 1)NaCl \quad \Big\}$$
$$MgR_2 + 2n_sNaCl \rightarrow 2NaR + MgCl_2 + 2(n_s - 1)NaCl \quad \Big\}$$

$$(10.2)$$
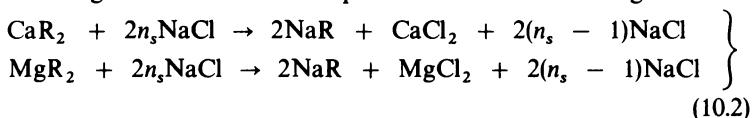
where n_s is the number of gram-equivalents of NaCl per g-equiv of replaced cations.

Stoichiometrically, n_s must be equal to 1 (i.e. 58.5 g/g-equiv). The value of n_s usually ranges from 2.5 to 3.5. It follows that $(n_s - 1)$ g-equiv of the reagent is wasted per gram-equivalent of replaced cations. That is why, in practice, various methods are used to reduce the loss of salt. These methods will be considered below.

10.1.2. Hydrogen Cation-Exchange Process

In hydrogen cation-exchange water softening, the exchange cation is hydrogen. The process involves the following reactions:

$$Na^+ + H^+R^- \rightarrow Na^+R^- + H^+$$
$$Ca^{2+} + 2H^+R^- \rightarrow Ca^{2+}R_2^- + 2H^+$$
$$Mg^{2+} + 2H^+R^- \rightarrow Mg^{2+}R_2^- + 2H^+$$
$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

$$(10.3)$$
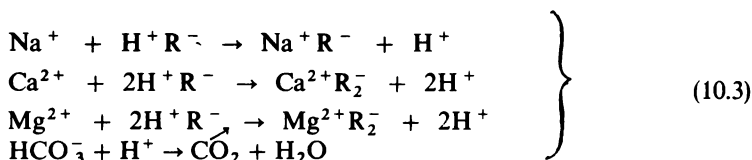
It is evident from these reactions that the H-exchange cycle removes completely the alkalinity of the water treated, with the result that the content of total solids in the water diminishes. The hardness of water treated by the H-exchange cycle falls to 10-15 μg-equiv/l and below. The salts of magnesium, calcium, sodium and of other cations pass into free acids since all cations are replaced by hydrogen cations. The H-exchange cycle thus changes not only the cation composition of the water treated, but also its anion composition since the ions, HCO_3^-, are removed from it. The total acidity of water softened by cation-exchange treatment will then be equal to the sum of the anions of mineral acids, Cl^-, SO_4^{2-}, NO_3^-, present in the initial water. Thus, water treated by the H-exchange cycle is acid and not suitable for use as feedwater in boiler units. In water-treatment plants the H-exchange cycle is always applied together with the Na-exchange cycle or with other water treatment processes. The advantage of the H-exchange cycle is that it permits a reduction in the alkalinity of the initial water.

An exhausted cation-exchange material is regenerated by passing through it a 1 to 1.5 per cent solution of sulphuric acid. Here hydrogen cations replace ions, Ca^{2+} and Mg^{2+}, that go into the solution and are removed from the softener. This process can be described by the following reactions:

$$CaR_2 + n_aH_2SO_4 \rightarrow 2HR + (n_a - 1)H_2SO_4 + CaSO_4$$
$$MgR_2 + n_aH_2SO_4 \rightarrow 2HR + (n_a - 1)H_2SO_4 + MgSO_4$$

$$(10.4)$$
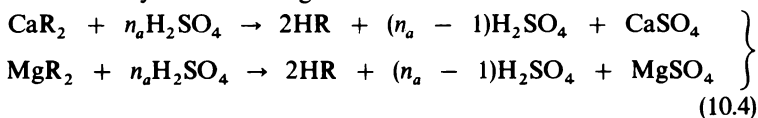
where n_a is the quantity of sulphuric acid, g-equiv, spent per g-equiv of the replaced cations.

In practice, n_a is within 1.6 to 2.0, i.e. about 80 to 100 g/g-equiv (at a stoichiometric value of 49 g/g-equiv).

10.1.3. Ammonium Cation-Exchange Process

The ammonium cation-exchange process has found application in treating water for industrial boiler houses. This method of water

treatment consists in that all cations present in the water being treated are replaced by ammonium cations, NH_4^+, as the water is filtered through the bed of cationite used for the purpose. The process can be represented by the following reactions:

$$\left.\begin{array}{l} Ca^{2+} + 2NH_4^+R^- \rightarrow Ca^{2+}R_2^- + 2NH_4^+ \\[2mm] Mg^{2+} + 2NH_4^+R^- \rightarrow Mg^{2+}R_2^- + 2NH_4^+ \\[2mm] Na^+ + NH_4^+R^- \rightarrow Na^+R^- + NH_4^+ \end{array}\right\} \quad (10.5)$$
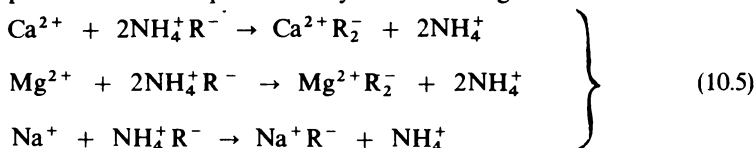
Thus, the softened water mainly contains ammonium salts, so that the hardness in waters treated by the ammonium cation-exchange process is insignificant.

The practical importance of this process stems from the peculiar behaviour of ammonium salts in cation-exchanger treated water and in boiler water. The softened water, containing ammonium salts, does not provoke acid reactions. Consequently, the apparatus and pipelines exposed to such water do not require anticorrosive protection. In boiler water, these salts undergo thermal decomposition with the formation of ammonia and acids:

$$\left.\begin{array}{l} NH_4Cl \rightarrow NH_3\uparrow + HCl \\[2mm] (NH_4)_2SO_4 \rightarrow 2NH_3\uparrow + H_2SO_4 \\[2mm] NH_4HCO_3 \rightarrow NH_3\uparrow + CO_2 + H_2O \end{array}\right\} \quad (10.6)$$
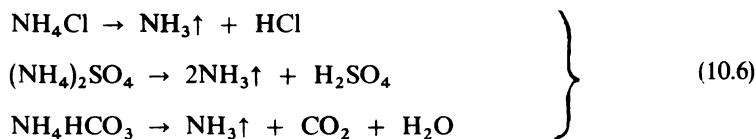
which must be neutralized by alkaline compounds:

$$\left.\begin{array}{l} HCl + NaOH \rightarrow NaCl + H_2O \\[2mm] H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2\uparrow + H_2O \end{array}\right\} \quad (10.7)$$
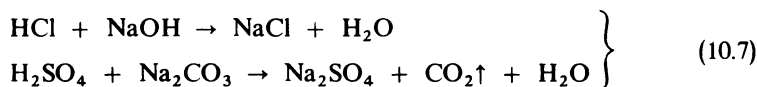
Consequently, the water treated by the ammonium cation-exchange process is potentially acid and cannot be used as feedwater for boiler units. That is why the ammonium cation-exchange process is practiced in water treatment plants only in conjunction with the sodium cation-exchange process.

An exhausted ammonium cation-exchange softener is regenerated with ammonium sulphate, $(NH_4)_2SO_4$. Depending on the layout of the ammonium and sodium cation-exchange plant (parallel or combined operation of the sodium cation-exchange and ammonium cation-exchange units), the regenerant solution must contain either ammonium sulphate alone or a mixture of $(NH_4)_2SO_4$ and NaCl

taken in a definite proportion. The basic shortcoming of the process being considered is an appreciable enrichment of the generated steam with ammonia; a high concentration of this chemical in condensate causes corrosion of copper alloys in the presence of oxygen. This water-treatment method has found limited application.

10.2. Characteristics and Properties of Cation-Exchange Materials

At the present time sulphonated coal and synthetic materials, KУ-1 and KУ-2-8 types, are widely used as cation-exchangers in softeners operated at Soviet electric power stations. The sulphonated coal is manufactured by treating coal with sulphuric acid.

Cation-exchangers are characterized by a number of parameters, of which the most important are the operating exchange capacity, granulometric composition (grain size), bulk mass, swelling factor, and thermal stability. The most important quality characteristic of a cation-exchange material is its operating exchange capacity e, whose magnitude depends on certain properties of the material and operating conditions.

In an H-exchange cycle, the operating exchange capacity of sulphonated coal depends in the main on the composition of initial water. The anion composition of water, not affecting markedly the operating exchange capacity of the cation-exchange material in the course of sodium cation-exchange treatment, acquires decisive importance in hydrogen cation-exchange water softening.

In this case the operating exchange capacity of sulphonated coal grows with an increase in the content of ions, HCO_3^-, in the initial water, i. e. with an increase in the ratio between equivalent values of HCO_3^- and $HCO_3^- + SO_4^{2-} + Cl^- + NO_3^-$. The KУ-1 and KУ-2 cation exchangers do not show such properties as is clear from Fig. 10.1

The operating exchange capacity also depends on the concentration in softened water of cations similar to the exchange cation. An increase in this concentration causes a decrease in exchange capacity. This means that initial water with a high salt content ($\geqslant 800$ mg/l) cannot be softened sufficiently in one softener by using an economically reasonable amount of regenerants.

This is due to the so-called counterion effect, the essence of which comes to the following. When water with a high salt content (concentration) passes through, say, a bed of sodium cation-exchange
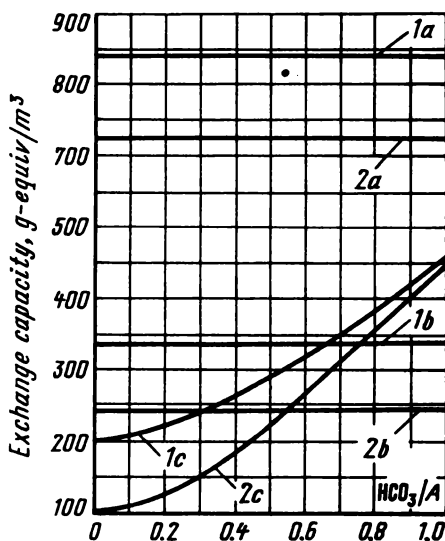
Fig. 10.1. Exchange capacity of cation-exchange materials as a function of initial water quality (with a consumption of H_2SO_4 equal to 2.5-3.0 g-equiv/g-equiv)

1 — total salt content of initial water is 1 mg-equiv/kg; *2* — total salt content of initial water is 15 mg-equiv/kg; *a* — cation-exchange material KУ-2; *b* — cation-exchange material KУ-1; *c* — sulphonated coal

material, the concentration of ions, Na^+, in the water grows as it flows downward because the ions replace cations Ca^{2+} and Mg^{2+}. The concentration of ions, Na^+, becomes maximum in the bottom part of the bed. The increased concentration of counterions (Na^+ in this case) suppresses dissociation of the cation exchanger and decelerates the ion-exchange process. In the event of hydrogen cation-exchange treatment, such deceleration intensifies with a decrease in the fraction of ions, HCO_3^-, of the total sum of anions present in the water treated.

The exchange capacity of a cation-exchange material is affected materially by the nature of cations being absorbed. Any cation may be fully absorbed by the cation-exchange material, but the operating exchange capacity will depend on the nature of the particular cation. In the series of cations, $Na^+ < NH_4^+ < K^+ <$

$< Mg^{2+} < Ca^{2+}$, each subsequent cation is absorbed more intensively than the preceding one. Accordingly, the sodium exchange capacity of sulphonated coal about 1.5 times smaller than its calcium exchange capacity (180 and 280 g-equiv/m^3 respectively). The Na and Ca exchange capacities of КУ-1 and КУ-2 differ but little.

The opposite is also true for the foregoing series of cations: every preceding cation will be replaced in the cation-exchange material by the subsequent cation if the two cations are present in the solution in comparable concentrations. This fact shows that the cation-exchange process features a somewhat peculiar nature, which can best be understood by referring to Fig. 10.2; it presents graphically the process of hydrogen cation-exchange treatment of a solution containing cations, Na$^+$ and Ca^{2+}.
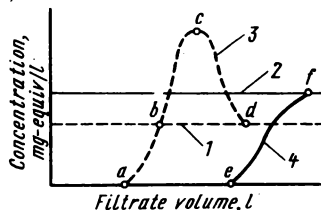
Fig. 10.2. Treatment of a solution containing Ca^{2+} and Na$^+$ by the hydrogen cation-exchange process

1 — sodium concentration in initial water; 2 — calcium concentration in initial water; 3 — sodium concentration in filtrate; 4 — calcium concentration in filtrate

Complete absorption of all cations takes place up to point *a*. At point *a* sodium cations appear (onset of breakthrough) in the softened solution. At point *b* the concentration of Na$^+$ in the filtrate becomes equal to that in the initial solution, which indicates that the cation-exchange material does not absorb the cation. Further away from point *b* the cation, Ca^{2+}, begins to replace Na$^+$ in the cation-exchange material and its concentration in the filtrate exceeds that in the initial solution. As it passes through a maximum (point *c*), the concentration of sodium becomes equal to the initial value at point *d*, i.e. the process of its replacement in the cation-exchange material terminates. At point *e* breakthrough of calcium cations is observed, which rises in intensity up to point *f*. In

practice such a stepped hydrogen cation-exchange process leads to a change in the acidity of treated water.

Cation-exchange materials swell in water. The extent to which they grow in volume is specified by the swelling factor. In this connection, the bulk mass, t/m^3, of a commercial, swollen (in water), and dry cation-exchange material is distinguished. The amount of commercial cation exchanger required for one cation-exchange softener can be calculated by the formula

$$q_c = \frac{fhm}{k} \tag{10.8}$$

where f = cross-sectional area of cation-exchange softener, m^2
h = height of cation-exchanger bed, m
m = bulk mass of commercial cation exchanger, t/m^3
k = swelling factor

Swelling of cation-exchange materials must be taken into account in charging them into cation-exchange softeners. Otherwise, the cation exchanger bed will be rather high and the ion exchanger will be carried away from the softener on loosening. Sulphonated coal is capable of operating in water with pH $\leqslant$ 7.5 at a temperature below 353 K without appreciable peptization. At pH above 8.3 and t over 343 K, sulphonated coal peptizes and imparts the filtrate a yellowish colour. The KУ-1 material shows higher thermal endurance. The KУ-2-8 type hydrogen cation exchanger withstands a temperature of 383 to 393 K.

The numerical values of some characteristics of cation-exchange materials are given in Table 10.1.

The KУ-2-8 type cation exchanger is comparable in properties to the following foreign grades: Amberlite IR-120, Dowex (USA), Zerolit-225 (Great Britain), Wofatit KPS-200 (GDR), Varion KS (HPR).

10.3. Operation and Regeneration of Ion-Exchange Softeners

10.3.1. Operating Cycle of Ion-Exchange Softeners

The operation of an ion-exchange softener includes the working stage, in which the water is ionized, and the regeneration stage. Let us consider the operation of a sodium-cation exchange water

Table 10-1

Quality Characteristics of Cation-Exchange Materials

Grade	Grain size, mm	Bulk mass of cation-exchange material, t/m^3		Exchange capacity, g/equiv/m^3		Moisture content, %	Swelling factor, k	
		commercial	swollen	Na-cation exchanger	H-cation exchanger		dry	commercial
Sulphonated coal	0.3-1.5	0.65	0.82	350	270	≤30	1.8	1.25
KY-1	0.3-1.5	0.7	0.7	350	350	50-60	2.0	1.0
KY-2-8	0.3-1.25	0.75	0.75	950	650	50-60	2.1	1.0

softener. All the basic conclusions we shall arrive at here will be valid for all ion-exchange processes.*

The process of water softening in a cation-exchange unit is presented graphically in Fig. 10.3. Point D represents the hardness in the initial water. It takes some time to soften a given volume of initial water. The softening process is started when the treated
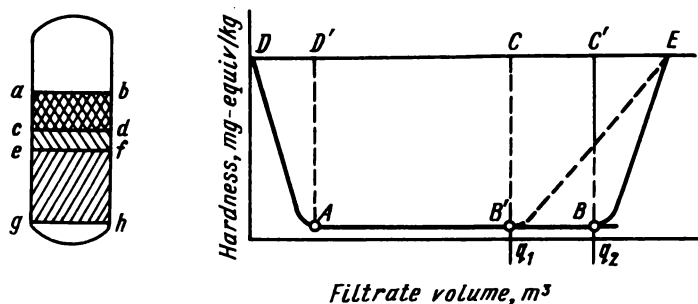
Fig. 10.3. Water treatment in a cation-exchange softener

water comes into contact with the cation-exchange bed and terminates somewhere in the bed. The layer of the cation-exchange bed in which water softening is started and completed is called the working layer or the softening zone, whose height depends on many factors.

In the course of operation of a softener, the upper layers of the softening zone become exhausted and can no longer participate in the ion exchange process. Water is then softened in the fresh underlying layers of the cation-exchange bed. In this way the softening zone moves downward gradually. Some time after the softener has been set to work, three zones form in the cation-exchange bed, namely the working (c-d-f-e), the exhausted (a-b-d-c), and the fresh (e-f-h-g) zone of the cation-exchange material.

The softener is put into operation at a rather small hardness (point A in Fig. 10.3), which remains practically constant until the lower boundary of the working zone (e-f) coincides with the bottom layer of the cation-exchange material (g-h). At the moment of coincidence (point B), cations of scale-making elements break through (i. e. cations, Ca^{2+} and Mg^{2+}, appear in the filtrate and grow in number), and the hardness in the softened water begins to

increase until it gets equal to that in the initial water at point E. This is indicative of complete exhaustion of the cation-exchange material. Since the purpose of the sodium cation-exchange process is water softening, the softener is taken out of service for regeneration at point B, i. e. before filtrate hardness increases to an inadmissible value.

The area $ABCD'$ (Fig. 10.3), denoted by E, g-equiv, is equivalent to the number of cations replaced in the softener and referred to as the operating exchange capacity of the softener (i. e. of the cation-exchange material charged into the softener). Disregarding the hardness in the softened water, which is quite admissible to do in the given case, we can write

$$E = H_t q_2 \tag{10.9}$$

on the other hand

$$E = eV \tag{10.10}$$

whence

$$E = ehf \tag{10.11}$$

It follows that

$$e = \frac{H_t q_2}{hf} \tag{10.12}$$

where h = height of the cation-exchange bed, m
   f = cross-sectional area of cation-exchange softener, m^2
   q_2 = quantity of softened water, m^3
   V = volume of cation-exchange material charged into the softener, m^3

Denoting the rate of water flow through the softener by v, we can write

$$q_2 = vfT = \frac{ehf}{H_t} \tag{10.13}$$

whence the time the cation-exchange softener is kept in operation between two successive shutdowns, T, called the interregeneration time, can be calculated by the formula

$$T = \frac{eh}{H_t v} \tag{10.14}$$

The interregeneration time must be within 12 h. For small water-treatment units, it may be prolonged to 24 h.

The area of triangle *BCE* characterizes the exchange capacity of the nonutilized zone of the cation-exchange bed, referred to as the residual or tail exchange capacity, which is a minimum only when the planes that confine this zone are horizontal. In practice, due to a number of reasons, the operating zone can be confined by curved planes. Then the breakthrough of scale-making compounds sets in well before the prescribed time. This moment is presented on the exhaustion curve by point *B'*. As a result the utilized bed exchange capacity (area *AB'C'D'*) decreases due to an increasing residual capacity (area *B'EC'*). That is why in practice measures are taken to have softeners loaded uniformly over the entire cross-sectional area. A rather flat exhaustion curve (as curve *B'E*, for instance) plotted for a given softener is indicative of the unsatisfactory hydrodynamic characteristic of the softener. This defect calls for inspection of the softener and discharge of the exchange material.

A cation-exchange softener is kept in service until the bed is exhausted (up to point *B*); the extent of exhaustion is determined by the hardness (or another characteristic) of the softened water. The exhausted softener is taken out of service and regenerated.

The foregoing is the description of theoretically possible operation of a cation-exchange softener. In practice, due to a number of reasons, the boundaries of the operating zone may be distorted to a greater or lesser extent. Then, the breakthrough of the cations destined for replacement will start earlier than it is anticipated (for instance, at point *B'*, Fig. 10.3), and the water softening cycle will have poorer characteristics.

10.3.2. Straight-Flow Regeneration of Ion-Exchange Softeners

Straight-flow regeneration is the process in which the dissolved regenerant is passed through the exchange bed in the same direction as the treated water. Regeneration of an ion-exchange softener involves the following successively carried out operations: backwashing, regeneration proper, rinsing the softener with the rinse water discharged into the drain, and rinsing with the rinse water discharged into a tank. In some cases the last two operations are combined and the water used for rinsing is discharged into the sewerage.

In backwashing, wash water is passed through the ion-exchange softener via valve *4* (Fig. 10.4). After the upflowing water passes through the ion-exchange bed, it is discharged into the sewerage through valve *3*, which is opened slowly until the preset backwash-ing rate is ensured. Backwashing brings the ion-exchange material to the suspended state. The purpose of the process is to do away with local compact portions formed in the bed during the preceding softening run and thus improve the hydrodynamic properties of the
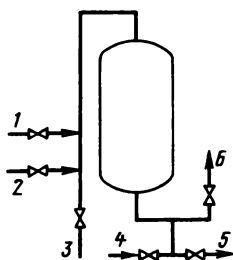
Fig. 10.4. Piping system of an ion-exchange softener

exchanger and also to remove the impurities carried into the softener with water and the products of disintegration of the exchang-er particles. For this to be accomplished, backwashing should be conducted at a certain rate of water flow, 3.0 or 4.0 $1/m^2$ s (the linear velocity of water flow is 9 to 13 m/h). The operation lasts 10 to 15 min.

After the backwashing operation is over, regeneration proper is started. A solution of the regenerating chemical of definite concentration and in the required amount is fed into the softener from above downward through the cation-exchange bed. Regeneration is initiated and conducted by opening valves *1* and *5*. After it passes through the cation-exchange bed, the regenerating solution is discharged into the sewerage. The rate of regenerant flow through the cation-exchange bed is usually equal to 4 or 5 m/h when salt is used as a regenerant, and 9 or 10 m/h when regeneration is done with sulphuric acid. Sodium cation-exchange softeners are regenerated with a 6 to 8 per cent solution of NaCl, and hydrogen cation-exchange softeners with a 1.0 to 1.5 per cent solution of H_2SO_4. The consumption of regenerant, kg, per regeneration of an ion-exchange softener can be calculated by the

formula

$$q_r = \frac{ehf\gamma_r}{1000} \tag{10.15}$$

where γ_r is the specific consumption of the regenerant, g, per g-equiv of the operating exchange capacity of the ion-exchange material.

In calculations the consumption of NaCl and H_2SO_4 may be assumed equal to 180-200 and 80-100 g/g-equiv, respectively. The amount of regenerant consumed affects materially the exchange capacity of the cation-exchange material and the residual concentration of the absorbed ion in the filtrate (softened water).

After the regenerant solution is fed to the softener and passed through the cation-exchange bed during 20 to 30 min, the third operation, rinsing of the softener, is initiated. For this purpose valve *1* is closed and valve *2* opened. Rinsing is conducted at a rate of water flow equal to 4 or 5 m/h and 9 or 10 m/h in the event of salt and acid regeneration, respectively. When the quality of rinsing water leaving the softener meets the standard requirements, valve *5* is closed, valve *6* is opened and the softener is put into operation. It takes 1.5 to 2.0 hours or more to regenerate the exhausted ion-exchange water softener.

10.3.3. Counterflow Regeneration of Ion-Exchange Softeners

Regeneration is of great importance in improving the performance of ion-exchange softeners. The process should ensure a maximum possible removal from the ion-exchange material of the ions absorbed in the bed during the preceding softening run at a minimum consumption of the regenerant. But it is practically impossible to meet this requirement with common straight-flow regeneration (Fig. 10.5a) since one cannot remove from the bottom layers of the bed all the ions (for instance, Ca^{2+}, Mg^{2+}, Na^+).

When a straight-flow regenerated softener is put into operation, the retained cations will be replaced by the hydrogen ions contained in the first portions of the water softened by the H-exchange cycle. These cations will deteriorate the quality of the softened water. The quantity of the contaminating ions entrained by the softened water is referred to as *breakthrough*, C_{br}, mg/kg, which

is determined by the equation

$$C_{br} = S\cfrac{1}{1 + \cfrac{K\eta_r}{100 - \eta_r}} \qquad (10.16)$$

where S = concentration of removed ions in treated water, mg/kg
K = coefficient characterizing the distribution of ions between the ion-exchange bed and water
η_r = degree of regeneration, %
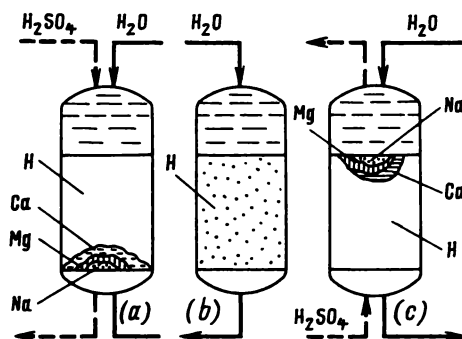
Fig. 10.5. Regeneration methods for hydrogen cation-exchange softeners

(a) straight-flow; (b) straight-flow with mixing of the ion-exchange material; (c) counterflow

It follows from Eq. (10.16) that to reduce the amount of breakthrough at a given K it is necessary to decrease S or increase η_r. It is not always possible to reduce S. That is why the only feasible way left is to increase in every possible manner the degree of regeneration, expecially that of the bottom layers of the ion-exchange bed with which the treated water is in contact before leaving the softener. This can be ensured by several methods.

The known method of increasing the degree of regeneration, η_r, is based on regeneration of the ion-exchange bed with a large amount of surplus regenerant. It is, however, not advisable to follow this uneconomical method, which also involves the discharge of a great amount of the reagent with the waste water. With the second method, the ion-exchange bed is mixed up by compressed air, water or an air-water mixture after its straight-flow regene-

ration. The ions retained in the bottom layers of the ion-exchange bed are then scattered over the entire volume (Fig. 10.5*b*) so that these layers become, as it were, deeply regenerated. The third and most effective way of raising the degree of regeneration is to effect counterflow regeneration (Fig. 10.5*c*): the acid is passed through the bed in upward flow, and the water in the opposite direction, with the result that the bottom layers of the ion-exchange bed undergo high-degree regeneration. To ensure large values of η_r at the softener outlet, the ion-exchange bed must be rinsed after counterflow regeneration with softened water and the same water must be used in preparing the solution of reagents. Otherwise, all the advantages of counterflow regeneration cannot be used. When properly realized, this method enables high-quality water softening at a minimum consumption of regenerants.

10.4. Preparation of Salt and Acid Solutions

For small-capacity water-treatment plants, the regenerating solution is usually prepared in brine tanks. The general view of such a tank is shown in Fig. 10.6. Salt is charged into the brine
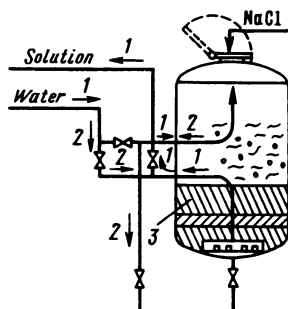
Fig. 10.6. General view of brine tank (saturator)

1 — water flow for salt dissolving; *2* — water flow for washing the brine tank; *3* — filter

tank in the quantity required through a large handhole. In some of the brine tanks the handhole is replaced by an opening with a damper. Since salt often contains various impurities, a bed of crushed anthracite or quartz sand is provided in the tank to make possible clarification of the brine. After salt is charged into the tank, clarified water is delivered into it to prepare the brine. The process of salt charging into a brine tank is being presently mechanized.

The above described method of preparing brine for regeneration is not suitable for large-capacity water-treatment plants. Consumption of great amounts of salt for one regeneration (800 to 1000 kg and more) requires the use of large-size brine tanks. In addition, the presence of the brine tanks in the layout hampers mechanization of the operations involved in brine preparation. The concentration of the brine leaving the brine tank varies: the first portions are saturated, and the last are strongly diluted, for which reason regeneration of the cation-exchange bed is impaired. To do away with these shortcomings, large water-treatment plants are fitted with wet-salt storage basins (or tanks) depicted in Fig. 10.7. A large amount of salt (150 to 250 t) is charged from dump trucks or directly from railway cars into reinforced concrete storage tanks *1* that are then filled with water. Thus, the wet-salt storage tanks always contain a required quantity of saturated brine. The brine is
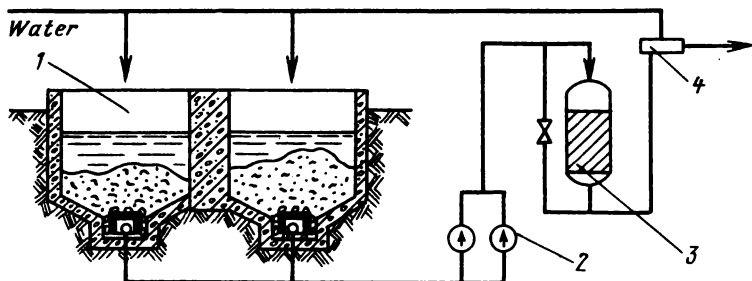
Fig. 10.7. Wet-salt storage facilities

drawn by pumps *2*, then clarified in clarifier *3*, diluted to required concentration in mixer *4* and delivered to the softener being regenerated.

Another layout for wet-salt storage, shown in Fig. 10.8, has no brine-handling pumps: the saturated brine flows by gravity into brine measuring tanks *4*, from which water ejectors *3* draw the brine and deliver it to softeners. The brine is diluted to required concentration in the ejectors. The brine in tank *1* is maintained at the preset level by float-type level controller *2*.

At the present time it is considered inexpedient to furnish even small-capacity water treatment plants with salt tanks. Instead, wet-salt storage is organized and the regenerant brine is prepared
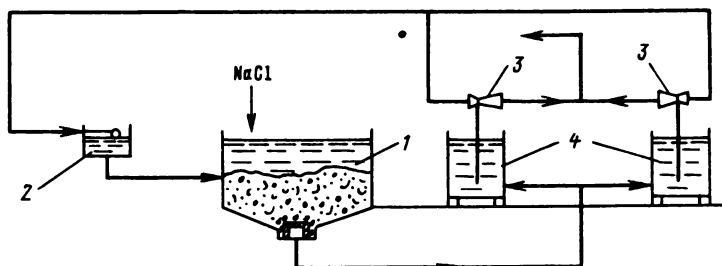
Fig. 10.8.. Wet-salt storage facilities. The solution is delivered by water-operated ejectors
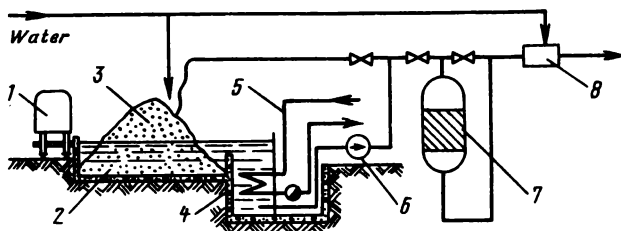
Fig. 10.9. Open wet-salt storage facilities

and delivered to softeners by means of water-operated, or water-jet, ejectors.

The layout of wet-salt storage facilities, most suitable for large-capacity water-treatment plants, especially for those located in severe climate regions, is depicted in Fig. 10.9. The wet-salt storage is a large rectangular cross-section tank, or basin, erected out of doors. Salt is discharged from cars *1* into basin *2* and a grab-bucket crane is used to arrange the salt in conical piles *3*. The salt solution flows into well *4* where it is heated in winter by heat-carrying agent *5*. Pump *6* is operated to deliver the warm solution to the pile of salt so as to dissolve it. The same pump delivers the brine via clarifier *7* to the softeners for their regeneration. The brine is diluted with water in mixer *8*. Dry-salt storage results in that the salt turns into monolith whose crushing involves great difficulties. The wet-salt storage layout depicted in Fig. 10.8 makes it possible to obviate these difficulties.

The operations involved in preparing an acid solution should be completely mechanized, and the acid should be handled with utmost care, observing all safety precautions. One of the variants of the layout that complies with these requirements is shown in Fig. 10.10. Acid is pumped from a tank-car into tank *1* by pump *9*. To make this possible, first valves *13* and *10* are closed and
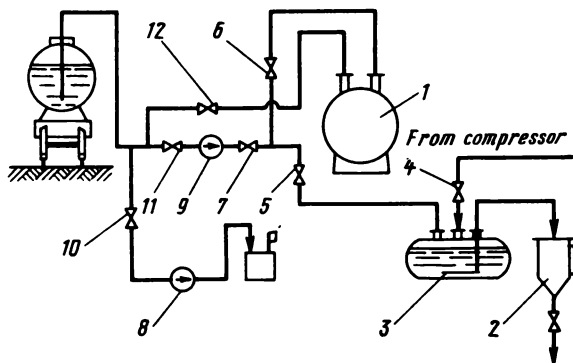
Fig. 10.10. Acid storage facilities

vacuum-pump *8* is put into operation. As a vacuum sets in the syphon-shaped pipe, acid flows from the tank-car into the pipe and primes pump *9*. Then, valves *11*, *7* and *6* are opened and pump *9* is put into operation. Acid is delivered from tank *1* into service tank *3* also by means of the pump with valves *12*, *11*, *7* and *5* opened (all the other valves are closed). The pump is also primed in this case by means of vacuum pump *8*. Acid is delivered from tank *3* into measuring tank *2* by displacing it from the tank with the aid of compressed air, fed into the tank through valve *4*.

10.5. Arrangement of Ion-Exchange Water Softeners

Illustrated in Fig. 10.11 is a vertical, pressure-type, single-bed, single-flow, first-stage, ion-exchange softener. It comprises cylindrical shell *6* and semispherical heads *2* and *4* secured to the shell by welding. In the centre of the heads there are holes for the influent (raw) and effluent (softened) waters. Air is evacuated from the exchanger through vent *9*. Pressure gauges *8* are used to
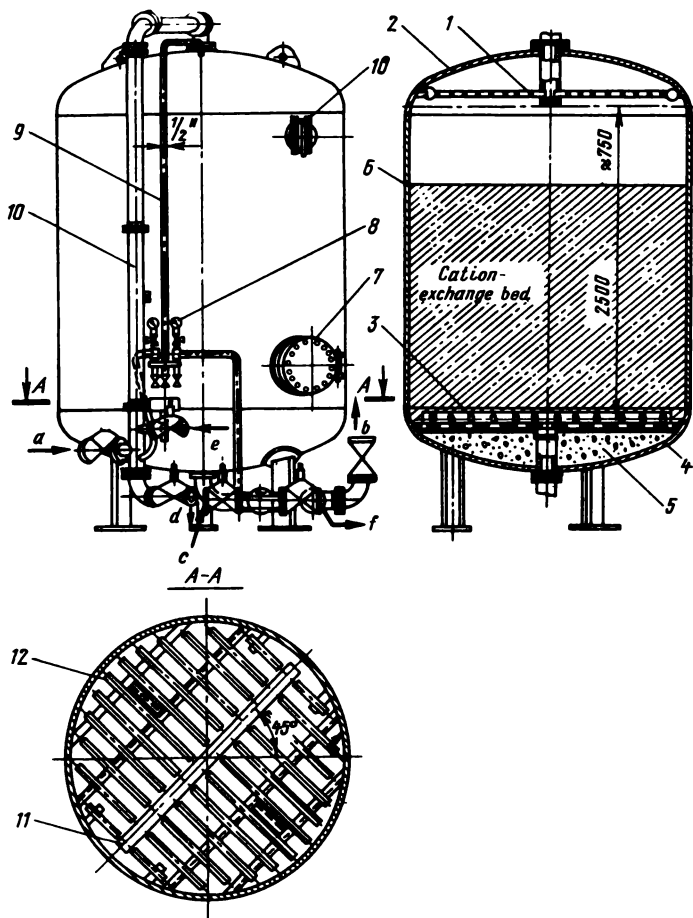
Fig. 10.11. Cation-exchange softener

a — influent inlet; *b* — effluent outlet; *c* — wash water inlet; *d* — wash water drain; *e* — dissolved regenerant inlet; *f* — rinse water drain

measure water pressure upstream and downstream of the softener. Manhole *10* permits examination of the softener and of the ion-exchange material (bed). Manhole *7* is used for inspection and repair of the underdrain system. The space above the cation-exchange

bed is filled with water during the operation of the softener. It is referred to as the rising space. This space permits expansion of the cation-exchange bed in washing by an ascending flow of water. The internal surface of the softener must be protected by a corrosion-resistant coating.

Inside the shell there are water distributing device *1* and underdrain system *3*. The upper distributing device and the underdrain system are designed to distribute raw water and collect the softened water uniformly over the entire cross-sectional area of the softener. The more uniform the distribution or collection of the softened water over the cross-sectional area of the softener, the better its operation, and the higher its efficiency characteristics.
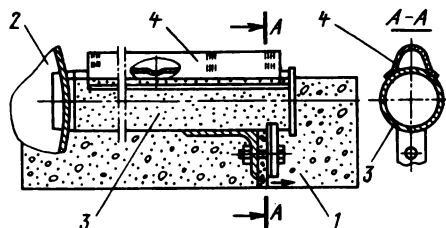
Fig. 10.12. Underdrain system

1 — concrete base; *2* — header; *3* — lateral arm; *4* — trough with 0.4 mm slots

The raw-water distributing devices and the underdrain systems may be of various designs. Presently underdrain systems of the header-lateral arms type are most widespread. The system of this type consists of header *11* placed on concrete base *5* provided in the bottom section of the softener. Perforated lateral arms (pipes) *12* are connected to the header. To keep fine particles of the ion-exchange material from leaving the softener through perforations, the lateral arms are covered with a slotted trough, as illustrated schematically in Fig. 10.12.

Figure 10.13*a* illustrates an underdrain system of the deflector-plate (false-bottom) type. It comprises a strong polymer plate clamped between flanges provided on the shell and bottom head. The holes in the polymer plate accommodate strainer heads. Compared to the header-lateral arms type, this underdrain system has a number of advantages, such as a smaller pressure drop,

a more uniform distribution (collection) of water, and a higher resistance to corrosion. An underdrain of the header-lateral arms type "copying" the shape of the lower head of the softener is illustrated in Fig. 10.13*b*. The merit of this underdrain system consists in that it requires no concrete base.
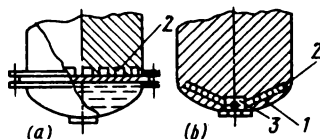
Fig. 10.13. Underdrain systems

(*a*) deflector plate "false bottom"; (*b*) "copying bottom"; *1* — header; *2* — lateral arm; *3* — distributing duct

10.6. Types of Ion-Exchange Water Softeners

10.6.1. Water Treatment Stages

In water-treatment plants, initial water passes through a number of various-purpose filters. First-, second- and third-stage softeners are distinguished. The water coming from the clarifying filters and tanks is treated in first-stage cation-exchange softeners (H_1, Na_1), which carry the greatest ion-exchange load, thereby they have a greater height and a thicker bed (2.0 to 2.5 m) of cation-exchange material. The bed in second-stage cation-exchange softeners and ion-exchange softeners is 1.5 m thick. First-stage ion-exchange softeners (A_1) also carry the main ion-exchange load. Second-stage softeners (H_2, Na_2, A_2) remove from the water the ions left after the first-stage treatment. If the treated water is to meet severe quality requirements, third-stage softeners (H_3, A_3) or mixed-bed units are provided for the plants to remove the remaining ions from the water. To ensure proper operation of the second- and third-stage softeners, they must be deeply regenerated, operated in the region of small ion-exchange loads and taken out of service before complete exhaustion of their exchange beds.

10.6.2. High-Capacity Water Softeners

The capacity, or throughput, of a water softener, q, is determined by the product of the filtration rate v and the filtering surface f, m^2,

i.e. $q = vf$. It follows that to increase q, either v or f, or the two quantities must be increased. In ion-exchange softeners, the rate of filtration is limited by the pressure drop through the bed of ion-exchange material, Δh, and by the time interval the equipment is kept in operation between regenerations, T. The pressure drop Δh increases and the time T decreases with growing v. Of course, it is desirable to operate softeners with a small pressure drop and a large value of T.

For softeners in which most of the ion-exchange reactions take place (first-stage units), it is most reasonable to increase the filtering surface. One can realize this in the following ways: (a) pass the water through a softener in more than one flow (multiflow softener), (b) provide inside a softener several chambers to be operated in parallel (multichamber softener), (c) ensure radial flow of the treated water in a softener (radial-flow water softener).

10.6.3. Multiflow Softeners

The multiflow water softener, shown in Fig. 10.14a, differs from a conventional (single-flow) unit in that it has no free space; the entire space inside the softener is filled with the exchange material. Two concentrically arranged main collectors are placed inside the exchange material: distributing collector 1 for the initial water and drain collector 2 through which the treated water is drained from the softener. Of the horizontal distributing and drain devices equi-distantly spaced over the height of the exchange material, the odd-number devices deliver the influent into the softener and the even-number devices discharge the effluent from the multiflow unit. For this reason the rate of water flow through the upper and lower distributing and draining devices is equal to one half that through the medium distributing and draining devices. In the softener of this design, it is possible to organize several separate flows of the water through the exchange material.

The capacity of the four-flow softener, shown in Fig. 10.14a, is equal to that of four single-flow units of the same diameter. An added advantage of this design is that the water softener proper can be mounted on top of roof 3 of the building intended to accommodate the control equipment. With this arrangement of equipment, the number of water flows can be increased substantially. The ion-exchange material can be regenerated by the counterflow technique, without the backwashing operation, which is

another advantage of this multiflow-counterflow type of softener. Periodically, every 1 or 2 months, as need arises, the exchange material is removed from the softener, loaded into a regenerator where the material is washed, freed of fine particles and regenerated. Where a multiflow unit is used as a clarifier, the filtering material is washed in a separately mounted regenerator.
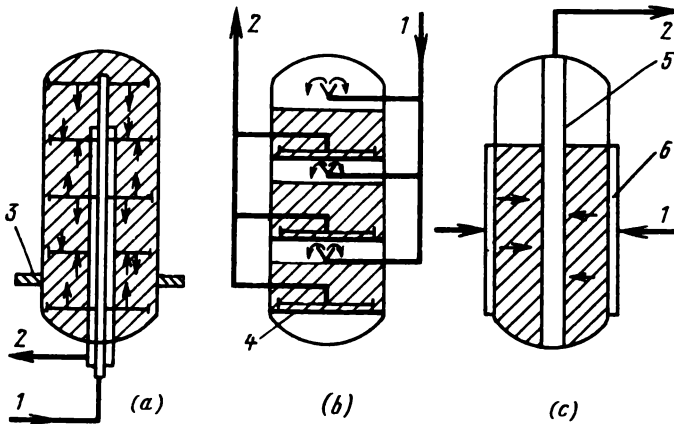
Fig. 10.14. High-capacity softeners

(*a*) multiflow; (*b*) multichamber; (*c*) radial flow

10.6.4. Multichamber Softeners

The volume of a multichamber softener (Fig. 10.14*b*) is separated heightwise by solid metal partitions 4 into separate chambers, each of which serves as a conventional single-flow softener with a rising space (water cushion). For this reason the number of chambers arranged in the softener of this kind will be smaller than the number of flows in a multiflow softener of the same height. Consequently, the throughput of this softener will be less than that of a multiflow unit. An advantage is that the multichamber softener can operate without an external regenerator.

10.6.5. Radial-Flow Softeners

Vertical tube 5 arranged along the centre line of the radial-flow softener, shown in Fig. 10.14*c*, carries a water distributing and

draining device. Another device of this type is arranged over shell 6 of the unit. The exchange material (ionite, sulphonated coal, crushed anthracite) is loaded into the annulus formed between the softener's shell and tube 5. Water 1 flows in radial streams into the softener and is drained off into main 2. Reliable performance of these softeners requires that the treated water should be delivered into it to press the ion-exchange bed. The rate of filtration varies here: it increases toward the centre line.

10.6.6. Continuous Ion-Exchange Units

Continuous ion-exchange units have come into being owing to the efforts made by designers and researchers to create high-capacity water-treatment equipment. The continuous ion-exchange units operate at high rates of filtering (up to 100 m/h) with a minimum consumption of reagents, produce high-quality water and require a relatively small-size bed of ion-exchange material. Several designs and layouts of continuous water-treatment plants are available. In some of them the ion-exchange material moves continuously in a closed circuit, in others it moves periodically or remains at rest while the water and the reagents are set in motion. All these layouts have their merits and shortcomings. The most popular continuous water-treatment equipment of this kind is fabricated by the Japanese company Asachi and the French company Degremont, which has improved the Japanese design. A similar modification, elaborated in the USSR, is shown schematically in Fig. 10.15.

A continuous ion-exchange unit usually consists of several apparatus designed to perform definite operations involved in the water treatment cycle, such as regeneration, rinsing, ion-exchange softening, etc., which are partly or fully accomplished in one apparatus. The design shown in Fig. 10.15 incorporates two columns: main, 1, and auxiliary, 6. Distributing devices 2 divide column 1 into four zones: zone A for water softening, for instance; zone B where the ion-exchange bed is freed from regeneration products by washing; zone C for regeneration, and zone D for reloading. In column 6 the ion-exchange material is freed from fine particles and impurities by washing. In addition to the columns, the water-treatment units may incorporate reagent-preparing and storing facilities, pumps and pipelines. Each continuous ion-exchange unit is a self-contained high-capacity plant. All operations

involved in the water-treatment cycle are automatically controlled since the continuous softener cannot be manually operated.

The continuous ion-exchange unit depicted in Fig. 10.15 performs as follows. Initial water *8* is delivered at the bottom of the apparatus at a rate of Q_i, m³/h, passes through zone *A* and leaves softener *9* at a rate of Q_e. An amount of water, equal to $Q_i - Q_e$, m³/h, passes into zone *B* and further into zone *C*. At the end of zone *B*, dissolved reagent *3* is introduced into the softener. The
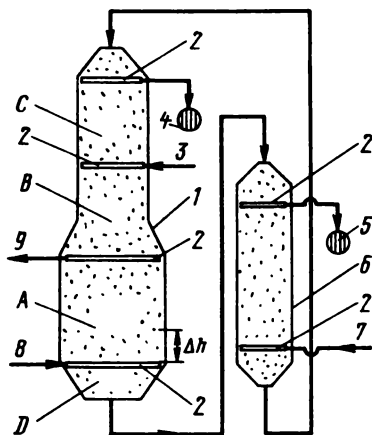
Fig. 10.15. Continuous ion-exchange unit

waste solution is removed into drain *4*. It will be noted that layer *A* of the ion-exchange material is clamped and the material in zone *C* is adequately regenerated. These features make it possible to operate the unit at high rates of water flow and obtain high-quality water.

After a certain time (about 20 to 40 min), when the bed of ion-exchange material becomes exhausted over, say, height Δh, the operation is interrupted for 20 to 30 s, during which time the exhausted volume of the ion-exchange material is passed into chamber *D* and the vacant volume in chamber *A* is filled with the regenerated ion-exchange material from chamber *B* that is later charged with the regenerated, but not washed, ion-exchange material from chamber *C*. After accomplishing these operations, the unit is put into operation. Then, the exhausted ion-exchange

material is displaced hydraulically from chamber *D* into column *6*, where the material undergoes washing to remove fines from it. An appropriate amount of the ion-exchange material is delivered into column *1*. Wash water *7* is removed from the softener together with impurities into drain *5*. This terminates one water-treatment cycle and another cycle is started.

10.6.7. Counterflow Softeners

The main difficulty that arises here is that the upflowing water expands the bed of the ion-exchange material and thereby inadmissibly impairs ion-exchange water softening. That is why counterflow softeners must be fitted with special devices or with a system of piping that would eliminate this drawback. Several designs of such devices have been presently suggested and patented.

Designs of counterflow water softeners are shown in Fig. 10.16. The ion-exchange bed in the softener shown in Fig. 10.16a is squee-
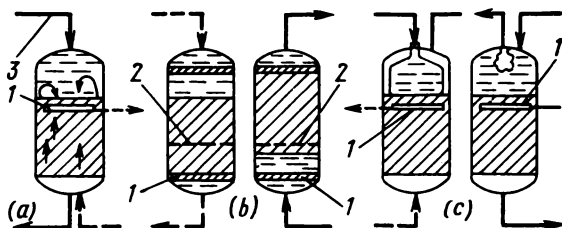
Fig. 10.16. Counterflow softeners

zed hydraulically since the upflow of reagent solution leaves it through medium underdrain system *1* immersed in the ion-exchange bed to a depth of 200-400 mm. The bed cannot expand since there is no flow through the water space of the softener. In reality, however, the ion-exchange bed is not squeezed sufficiently because the liquid can flow through the water space as shown by the arrows in the illustration.

Better results are obtained when the ion-exchange bed is "locked" by a small flow of softened water · *3* being forced during regeneration from top downwards and drained off through underdrain system *1*.

The softener shown in Fig. 10.16*b* is regenerated by a downflow of reagent solution. At the same time the water flows upward at a sufficiently high rate, lifts and presses the ion-exchange material against the upper distribution device. Grid *2* facilitates squeezing of the ion-exchange material. In the design shown in Fig. 10.16*c*, the bed is squeezed by a "flask" of elastic material inserted into the space on top of the bed. In counterflow regeneration, the flask that receives the water under pressure increases in size and prevents expansion of the ion-exchange bed. The waste regenerant solution is removed from the softener through underdrain system *1*. When the softener is in operation, the water is displaced from the flask so that its size diminishes drastically and the flask does not affect ion-exchange softening.
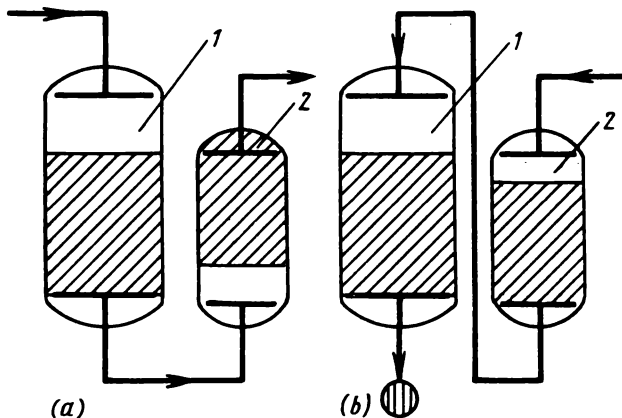
Fig. 10.17. Two-stage counterflow ion-exchange softener

(*a*) water softening run; (*b*) regeneration

Figure 10.17 illustrates a two-stage counterflow ion-exchange softener. To provide for deep regeneration of a small part of the ion-exchange bed that comes in contact with the water leaving the softener, the entire ion-exchange material is located in two vessels of different capacity: about $\frac{2}{3}$ of the material is in vessel *1* and $\frac{1}{3}$ in vessel *2*. The water flows downward through vessel *1* (first stage) and then moves to vessel *2* (second stage) in upflow. Since the water velocity in the second stage is not less than 30 m/h, the ion-ex-

change bed lifts and presses against the top head, and thereby becomes properly squeezed.

The regenerant solution required for treating the entire ion-exchange material in the softener is first directed in upflow through the second stage, then through the first stage in the same direction. The second stage is washed by softened water. Softeners of this kind consume a rather small amount of reagents, 1.2 to 1.5 g-equiv/g-equiv, and give high-quality filtrate.

10.7. Attendance of Cation-Exchange Water Softeners

Cation-exchange softeners must be operated so as to obtain the water of preset quality with the smallest possible consumption of reagents. As mentioned earlier, to ensure a most complete removal of cations from water, in particular to effect water softening, the part of the cation-exchange bed that is in contact with the water leaving the softener should be very deeply regenerated by applying the methods treated of in Sec. 10.3.

Regeneration usually begins with backwashing, i. e. loosening the cation-exchange material by the upflow of water. The material expands and occupies almost the entire volume of the softener. This operation aids in removing impurities and disintegrated particles ($\leqslant$ 0.3 mm) from the ion-exchange bed. Experience shows, however, that it is not necessary to backwash the bed of exchange material before each regeneration. If the water being treated contains a small amount of mechanical impurities and the pressure drop through the bed does not grow, one can do without backwashing for a long time. Whenever the pressure drop through the ion-exchange bed exceeds 0.1 or 0.2 MPa or the total exchange capacity of the softener decreases (see Fig. 10.3), backwashing becomes a necessity. A decrease in the exchange capacity is usually observed when the hydrodynamic characteristic of the ion-exchange bed becomes unsuitable due to different reasons (clotting of the material, formation of "channels" through which most of the water flows, penetration of foreign matter; damaged underdrain system, etc.). Such a softener must be taken out of service, thoroughly inspected, and the ion-exchange material removed.

To ensure efficient operation of a cation-exchange softening plant, its exchange capacity should be kept at the highest level. Where this requirement is ignored, the performance of water

softeners deteriorates due to a variety of reasons, one of which is associated with poor coagulation of water in clarifying filters (of the straight flow type). The matter is that when the hydrolysis of an aluminium coagulant is incomplete, aluminium hydroxide can form on the grains of the cation-exchange material. It envelops the grains and isolates them from the water, with the result that the exchange capacity drops markedly and so does the efficiency of the plant. In addition, a greater amount of the reagent is spent. Deposition of calcium carbonate on the grains of the cation-exchange material has been found to yield similar results in two-stage liming and cation-exchange softening plants using unstable lime-treated water. The deposits formed in the cation-exchange bed are removed by rinsing it with an acid solution.

Carbon dioxide, CO_2, being formed during coagulation, reduces the pH of water, i. e. increases the concentration of hydrogen ions. Since they are capable of cation exchange, hydrogen ions react with the sodium cation-exchange material, draw off a fraction of the exchange capacity and thus reduce the operating exchange capacity relative to Ca^{2+} and Mg^{2+}. Two methods are used to increase the exchange capacity: CO_2 evolved in the process is either bound by treating the water with caustic soda upstream of the cation-exchange softeners or removed by blowing air through the water. The latter method can be easily realized in plants where an open hook-up is used to feed the coagulant into the tank upstream of the raw water pumps; the air can be blown through the water filling this tank. The exchange capacity of cation-exchange materials can also decrease due to other reasons, such as nonuniform water filtering over the entire cross-sectional area of the softener because of the crust of impurities formed on the surface of the bed. The presence of ammonia in the water being softened also reduces the exchange capacity of the cation-exchange material relative to scale-making matter.

As noted above, the amount of the reagent used for regenerating an ion-exchange material heavily affects the operating exchange capacity. In water-treatment practice, however, efforts must be made to reduce the specific consumption of the regenerant. Best results (1.2 to 1.5 g-equiv/g-equiv NaCl) can be obtained when using two-stage counterflow softeners (see Fig. 10.16). Continuous softeners require about the same amount of reagents. Stepwise regeneration with two reagent solutions of different concentration (first with a more diluted solution) and also with the use of wash

waters permits reducing the consumption of reagents to 2.0-2.6 g-equiv/
/g-equiv, and without the wash waters to 3.0-3.5 g-equiv/g-equiv.
The quality of sodium chloride (common salt) is also of importance.
The greater the content of calcium and sodium in the salt, the
poorer the regeneration of the cation-exchange material.

Review Questions

1. In an industrial boiler house, boiler water becomes acid periodically
when tested with a methyl orange indicator. What is the possible reason for
this phenomenon, taking into account the fact that the raw water delivered
to the sodium cation-exchange softener contains salts of ammonium?

2. Write down the main formula relating the rate of water filtration in
a cation-exchange softener to the height of the cation-exchange bed and the
time between regenerations. Describe its derivation.

3. 130 kg of dry cation-exchange material, grade KУ-2, is charged into
the softener 2.2 m high and 700 mm in dia. Is the calculated amount of the
material correct, considering that the swollen bed of the KУ-2 material is
1.5 m high?

4. What are the advantages of counterflow regeneration over straight-
flow regeneration?

Chapter 11

Cation-Exchange Water . Softening Plants

11.1. Sodium Cation-Exchange Water Softening Plants

Water treatment involves many technological processes that have been considered in the preceding chapters. The nature of these processes and the sequence in which they are applied may vary with the quality of initial water, the requirements imposed on the quality of softened water, the presence and availability of special water-treatment facilities and reagents, and so on. For this reason it is necessary to consider the layouts of water-treatment plants in which various combinations of technological processes are realized. These layouts usually receive their names from the technological processes that occur in succession.

Sodium cation-exchange water softening plants shown schematically in Fig. 11.1 find most extensive use at industrial boiler houses and power plants. The sodium cation-exchange softening plant illustrated in Fig. 11.1a is the simplest and cheapest. It comprises cation-exchange softeners and reagents-storage and preparation facilities. The water treated in this plant must be free of coarse-dispersed and colloidal impurities and also of ferric hydroxide. Many artesian waters and water from drinking-water supply mains meet these conditions.

The plant presented in Fig. 11.1b, with mechanical filters installed upstream of the softeners, is suitable for treating water that contains 80 to 100 mg/kg of suspended substances and also artesian waters contaminated by ferric impurities ($\geqslant$ 0.5 mg/kg). It is expedient to use this plant for treating surface waters contaminated periodically by coarse-dispersed substances that are well removed in clarifying filters.

The plant depicted schematically in Fig. 11.1c (for coagulation, mechanical filtering, and sodium cation-exchange softening) is more versatile, for it permits the removal of suspended and colloidal

substances. The water flows through the clarifying filters and cation-exchange softeners. A coagulant solution is delivered by metering pumps from a service tank into the pipeline upstream of the clarifying filters, and, if necessary, an alkaline solution is also introduced. The precipitating impurities are retained in the clarifying filters.
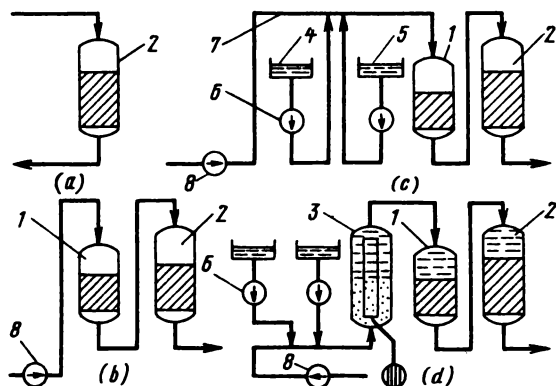
Fig. 11.1. Sodium cation-exchange plants

1 — mechanical filter; *2* — sodium cation-exchange softener; *3* — pressure clarifier; *4* — coagulant solution; *5* — alkali solution; *6* — metering pumps; *7* — water treated; *8* — pump

The plant depicted in Fig. 11.1*d* incorporates a sludge-blanket clarifier mounted upstream of the clarifying filters. The advantage of this plant consists in that it is capable of treating water with a high concentration of suspended substances (> 300 mg/kg), which greatly reduces the working load of the clarifying filters. With a coagulant and flocculants used, the water leaving the sludge-blanket clarifier can have a transparency of over 30 cm (as determined by the print method). It should be noted that during the most part of the year (8 to 10 months) the water of many surface sources contains an insignificant amount of colloidal impurities. Consequently, the coagulating facilities are operated only 2 to 4 months annually. Some waters, however, require year-round coagulation.

The layouts considered above are also called straight flow since

the water delivered by one group of pumps flows uninterruptedly through them. The basic demerit of these water-treatment plants is that they are incapable of reducing the alkalinity of the initial water. For this reason, when the maximum permissible values of alkalinity or the amount of total solids in boiler water, C_{bw}, are prescribed, these plants can be used for water treatment if the following condition is observed:

$$C_{iw} \leqslant \frac{p_s}{100 + p_s} \frac{C_{bw}}{\alpha_{ch}} 100 \qquad (11.1)$$

where C_{iw} = alkalinity, mg-equiv/l, or total solids, mg/l in the initial water
α_{ch} = chemically treated makeup for feedwater, %
p_s = calculated amount of blowdown for boiler units in relation to steaming capacity, %

In order that the relative alkalinity of boiler water should not exceed 20 per cent, the following inequality must hold

$$S_{iw} \geqslant 200 A_{iw} \qquad (11.2)$$

where S_{iw} = amount of total solids in initial water
A_{iw} = alkalinity of initial water

If condition (11.1) is not met, sodium cation-exchange softening alone should not be applied. Instead, use must be made of one of the decarburizing layouts to reduce the alkalinity and the total solids of initial water. Another approach is to reduce the factor α_{ch}, i.e. increase the fraction of condensate in feedwater.

11.2. Two-Stage Cold-Lime and Sodium Cation-Exchange Water Softening Plants

Water softening plants of this kind (Fig. 11.2) reduce the hardness, alkalinity, and the total solids of the initial water. Pump *1* delivers the water being treated to clarifier *2*, into which metering pump *3* feeds milk of lime drawn from mixing tank *4*. The water passes into intermediate tank *5*, from which a second group of pumps *6* delivers it to clarifying softeners *7* and further to sodium cation-exchange softeners *8* and *9* of the first and second stages, respectively. Plants of this kind are sufficiently versatile, capable of softening the water that contains mechanical and colloidal
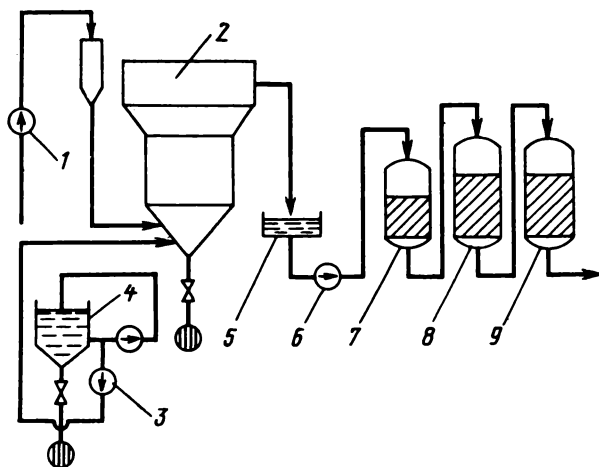
Fig. 11.2. Two-stage cold-lime and sodium cation-exchange water softening plant

impurities. The shortcoming of these water-treatment plants is that they need large-size clarifying filters and comparatively intricate lime-handling facilities.

11.3. Hydrogen Cation-Exchange and Sodium Cation-Exchange Water Softening Plants

Plants of this kind (Fig. 11.3) permit parallel, successive, and combined water softening by hydrogen and sodium cation-exchange processes. They are capable of reducing the alkalinity of the initial water, though to a different extent. In the water softening plant depicted in Fig. 11.3a, water is first treated in clarifying filters 1, from which it is forced in two flows to hydrogen cation-exchange softeners 2 and sodium cation-exchange softeners 3. If it is necessary to produce softened water with an excess alkalinity ΔA, the fraction (percentage) of water that must be directed to the hydrogen cation-exchange softeners, X_H, and to the sodium cation-exchange softeners, X_{Na}, will be determined by the expressions

$$X_H = \frac{A_t - \Delta A}{\sum An} 100; \quad X_{Na} = 100 - X_H \quad (11.3)$$

where $\sum An$ is the sum of all anions.

After it passes through the softeners, the acid water is mixed with the alkaline water treated in the sodium cation-exchange softeners so as to neutralize the free acids; the neutralizing reaction results; in binding hydrogen ions by bicarbonate ions:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O$$
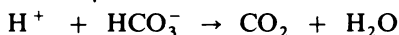
To remove the carbon dioxide being formed, the water is directed from the softeners to degasifier (desorber, decarbonizer) *4*. The
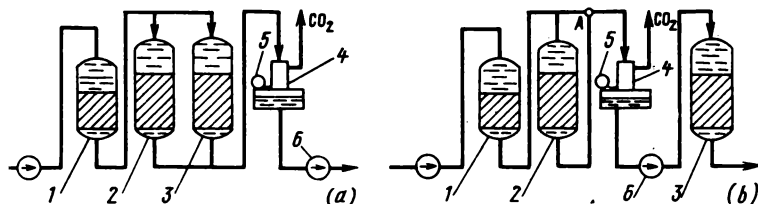
Fig. 11.3. Hydrogen and sodium cation-exchange water softening plants parallel (*a*) and successive (*b*) treatment with hydrogen and sodium cation exchangers

special packing of the degasifier is built up of ceramic rings. The air blown by fan *5* through the water flowing in films and droplets from the packing removes carbon dioxide. The air consumption amounts to 20-40 m³ per m³ of water. The residual concentration of CO_2 in the degasified water depends on water temperature and ies within 2 to 6 mg/l at the rate of air consumption specified above.

Plants used for water softening by means of parallel hydrogen cation-exchange and sodium cation-exchange processes usually handle slightly mineralized waters ($H_c/\sum An > 0.5$). The minimum alkalinity of water softened in plants of this kind is within 0.5 or 0.6 mg-equiv/l. It is more expedient to treat heavily mineralized waters ($S_{iw} = 1000$ mg/l, $H_c/\Sigma An < 0.5$) by successive hydrogen cation-exchange and sodium cation-exchange softening (Fig. 11.3*b*). From clarifying filters *1* the water passes to hydrogen cation-exchange softeners *2*. The acid water is neutralized due to the alkalinity

of the initial water as it is mixed with the latter at point *A*. Then the mixture passes into desorber *4*. The second group of pumps *6* delivers the degasified water to the sodium cation-exchange units *3* for final softening.

The combined hydrogen and sodium cation-exchange softening consists in that the cation-exchange material is first regenerated with a certain amount of acid, then, after rinsing, with a certain amount of salt. As a result, the cation-exchange material becomes charged with ions, H^+ and Na^+. As the water flows through the softener, hydrogen and sodium cation-exchange processes take place in the bed of the cation-exchange material. The hardness of water softened by the hydrogen cation-exchange process is 10 to 15 μg-equiv/kg or below.
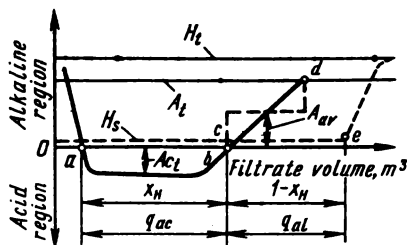
Fig. 11.4. Performance chart for hydrogen cation-exchange softener

The performance curve for a hydrogen cation-exchange softener from the moment of its operation (point *a*) is presented in Fig. 11.4. First the softener yields q_{ac}, m^3, of water with acidity $Ac_t = C_{SO_4^{2-}} + + C_{Cl^-} + C_{NO_3^-}$, mg-equiv/kg. Then, at point *b*, the acidity diminishes (due to breakthrough of sodium) and goes to zero at point *c*. From this time on the alkalinity increases and becomes equal to the initial alkalinity A_t at point *d*. During the alkaline cycle, from point *c* to point *d*, the softener produces q_{al}, m^3, of water with an average alkalinity A_{av}. Over this time interval the hardness of the cation-exchange treated water, H_s, is minimum and begins to increase (due to breakthrough of calcium) only at point *e*.

The amount of acid water that leaves the softener during the first period of operation can be determined by the formula

$$q_{ac} = \frac{\alpha\beta(B + 1)e^{Ca}fh}{(B + \beta\sigma)(C_{Na} + H_t)} \tag{11.4}$$

where σ = utilization factor for the sodium exchange capacity of the working bed of a *hydrogen cation-exchange softener when breakthrough of sodium takes place, $\sigma \approx 0.5$ or 0.6

β = ratio of the sodium exchange capacity of a cation-exchange material to the calcium exchange capacity; for sulphonated coal, $\beta \approx 0.5$ or 0.6; for the KУ-2 type cation-exchange material, $\beta \approx 1.0$

C_{Na} = concentration of sodium in the water treated, mg-equiv/kg

$B = C_{Na}/H_t$

h = height of cation-exchange bed, m

e^{Ca} = calcium exchange capacity, g-equiv/m^3

f = cross-sectional area of the softener, m^2

The amount of water softened in the unit during the softening run, m^3, prior to the breakthrough of hardness, is

$$Q_s = \frac{hfe^{Ca}}{H_t} \tag{11.5}$$

The fraction of acid water, x_H, yielded by the softener during the softening run amounts to

$$x_H = \frac{q_{ac}}{Q_s} = Ac_1 \frac{H_s}{C_{Na} + H_t}; \quad Ac_1 = \frac{(B + 1)\beta\sigma}{B + \beta\sigma} \tag{11.6}$$

During the second period of work the softener yields water of an average alkalinity

$$A_{av} = \frac{C_{Na}}{1 - x_H} - Ac_t \tag{11.7}$$

It follows from formula (11.4) that the smaller the value of C_{Na}, the more amount of acid water, q_{ac}, will be produced. If $Ac_t > C_{Na}/(1 - x_H)$, the alkaline cycle will not be observed in a hydrogen cation-exchange softener until after calcium breakthrough.

11.4. Hydrogen Cation-Exchange Water Softening Plants Operated with Deficient Regeneration

The fact that a hydrogen cation-exchange softener yields acid water during the first period of its operation complicates the maintenance of a water-treatment plant: pipelines must be

protected against corrosion, acid drains need neutralization, etc. These demerits are eliminated by regenerating the softener with insufficient amount of acid. This method, known as *deficient (starvation) regeneration* has found wide application. When the bed of a conventional hydrogen cation-exchange softener is regenerated, the entire cation-exchange material is converted into hydrogen cation-exchange material (Fig. 11.5a). This is due to the fact that an
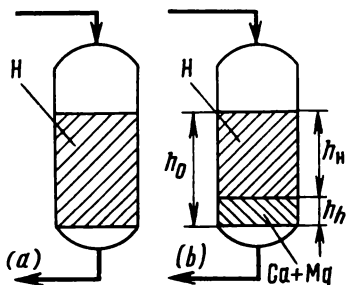
Fig. 11.5. Approximate   distribution of cations in cation-exchange bed

excess amount of acid is used for regeneration. A deficiency in the amount of acid results in a nonregenerated layer of calcium- and magnesium-cationites, h_h thick, left in the bottom part of the bed (Fig. 11.5b). The type of cation distribution shown in Fig. 11.5b differs from the actual distribution, but it is convenient for use in deriving some relationships.

In the H-cation-exchange layer h_H all cations become absorbed, $C = H_t + C_{Na} = Ac_t + A_t = C_{Cl^-} + C_{SO_4^{2-}} + A_t$, mg-equiv/kg. Instead, hydrogen ions appear, but in a lesser amount than C since a fraction of H^+ neutralizes ions, HCO_3^- :

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2\uparrow$$
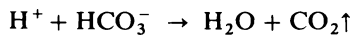
The quantity of such ions is $\Delta A = A_t - A_{tr}$, mg-equiv/kg, where A_t and A_{tr} denote the alkalinity of the initial and treated water, respectively. So, the amount of hydrogen ions that appear in the layer is

$$\sum H^+ = Ac_t + A_{tr}$$

These ions are replaced in the layer h_h by Ca^{2+}, Mg^{2+}, and Na^+, so that

$$q_{tr}(Ac_t + A_{tr}) = fh_h e^H$$

where q_{tr} = quantity of water treated for a softening run, m^3

e^H = average H-cation exchange capacity, g-equiv/m^3

f = cross-sectional area of the softener, m^2

Whence,

$$q_{tr} = \frac{fh_h e^H}{Ac_t + A_{tr}} \qquad (11.8)$$

On the other hand, the nominal H-exchange layer of the cation-exchange bed must treat the same amount of water, q_{tr}, and consequently

$$q_{tr}(Ac_t + A_t) = h_{Ca} e^{Ca} f + h_{Na} \beta e^{Ca} f = h_H e_{av} f$$

where e_{av} is the average exchange capacity of the layer h_H relative to Ca^{2+}, Na^+; $h_H = h_{Ca} + h_{Na} = h_0 - h_h$

Then,

$$q_{tr} = \frac{h_H e_{av} f}{Ac_t + A_t} \qquad (11.9)$$

Equating expressions (11.8) and (11.9) and solving for h_H, m, we obtain $e_{av} \approx e^H$, hence

$$h_H = \frac{Ac_t + A_t}{Ac_t + A_{tr}} h_h = \frac{(Ac_t + A_t)h_0}{\beta(Ac_t + A_t) + (Ac_t + A_{tr})} \qquad (11.10)$$

Knowing h_H, one can find the amount of acid, g-equiv,

$$q = \alpha h_H f e \qquad (11.11)$$

where e = operating exchange capacity of cation-exchange material

α = coefficient determined experimentally

Review Questions

1. The merit of a sodium cation-exchange plant is its simple design and layout. What are its main demerits?

2. Treated water is required for cooling a hot solution in a surface heat exchanger. The water was treated in a hydrogen and sodium cation-exchange softening plant. Why was this kind of plant selected for the purpose?

3. In a pilot water-treatment plant, initial water is first treated in a hydrogen cation-exchange softener, then in a sodium cation-exchange unit. Will the effluent from the sodium cation-exchange softener be acid?

Chapter 12

Demineralization of Water

12.1. Water Demineralization by the Ion-Exchange Demineralization Process

12.1.1. Anion-Exchange Treatment

Demineralization of water by the ion-exchange process involves ion-exchange treatment in addition to cation-exchange treatment considered above. The anion-exchange process is the exchange of anions between water-dissolved electrolytes and a solid granular material immersed in the water and referred to as an anion-exchange material (anion exchanger). The anion, OH^-, is usually used as an exchanger, although other anions can also be employed, for instance, Cl^-, CO_3^{2-}, HCO_3^-.

The anion-exchange process may be applied in treating water with various pH values. The process is most effective in handling an acid medium — water containing only hydrogen ions. For maximum removal of anions, the water is first passed through a hydrogen cation-exchange bed and then through an anion-exchange bed to replace the anions of acids by the exchange anion:

$$2R^+OH^- + H_2SO_4 \rightarrow R_2^+SO_4^{2-}$$
$$+ (2OH^- + 2H^+ \rightarrow 2H_2O)$$
$$R^+OH^- + HCl \rightarrow R^+Cl^- + H_2O$$
$$R^+OH^- + H_2SiO_3 \rightarrow R^+HSiO_3^- + H_2O \qquad (12.1)$$
$$R^+OH^- + H_2CO_3 \rightarrow R^+HCO_3^- + H_2O$$
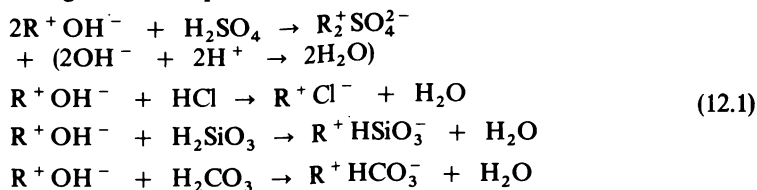
The above reactions result in almost complete removal of the anions of strong and weak acids and formation of weakly dissociating compounds, H_2O and CO_2. The formation of these compounds makes reactions (12.1) irreversible: they proceed only from the left to the right. This is an important property of the anion-exchange process. The cation-exchange process does not feature such a property. After replacement of all exchange anions,

OH^- or HCO_3^-, the anion-exchange material becomes incapable of absorbing anions from the water. The anion-exchange bed is regenerated by passing a regenerant solution through it. The process of regeneration can be conditionally described by the following formulae:

$$R_2SO_4 + 2n_{al}NaOH \rightarrow 2ROH + Na_2SO_4$$
$$+ (n_{al} - 1)\,NaOH$$
$$RCl + n_{al}NaOH \rightarrow ROH + NaCl + (n_{al} - 1)NaOH$$

$$(12.2)$$
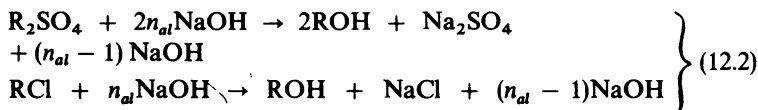
where n_{al} denotes the specific consumption of NaOH in g-equiv per g-equiv of the absorbed anions.

Theoretically, $n_{al} = 1$ (40 g/g-equiv), but practically, $n_{al} = 1.5$ to 2.5 for the AH-31 and 4 or 5 for the AB-17-8 type anion-exchange materials when all anions are absorbed. In this way a considerable amount of alkali is wasted. Various methods of regeneration are used to decrease the loss, though the results are not yet very satisfactory.

12.1.2. Anion-Exchange Materials

All anion-exchangers are synthetic materials. They are subdivided into two groups, weakly basic and strongly basic. The first are capable of absorbing the anions of only strong acids (SO_4^{2-}, Cl^-, NO_3^-) and cannot practically trap the anions of weak acids ($HSiO_3^-$, HCO_3^- and others). The materials of the second group are able to remove from aqueous solutions the anions of strong and weak acids. But they are usually more expensive and possess a smaller exchange capacity than weakly basic materials. Therefore, they are largely used for removal of silicic acid in plants of deep demineralization (in the second stage of the demineralizing system). Thus, two groups of materials are employed when complete demineralization of water is required.

Like cation-exchange materials, anion exchangers differ in exchange capacity. For most of the anion-exchange materials the relation $SO_4^{2-} > Cl^- > NO_3^-$ is valid. It shows that every preceding anion is absorbed more actively and in a greater amount than the following. Thus, for many anion-exchange materials the ratio between the operating exchange capacity with respect to the sulphate ion and the exchange capacity with respect to the chlorine ion falls within 1.4 to 1.5.

In contrast to cation exchangers, the exchange capacity of anion-exchange materials rises with the concentration of absorbed anions. This is due to the fact that counterions do not appear in appreciable amounts during the ion-exchange process, since the products of the ion-exchange reaction are weakly dissociated (H_2O, H_2CO_3).

An important characteristic of strongly basic anion-exchange materials is their *silica capacity*. The operating silica capacity is the amount of SiO_3^{2-}, g-equiv, absorbed by 1 m^3 of an anion-exchange material. It depends on the pH value of water, the initial concentration of SiO_3 in the water being treated, specific consumption of alkali for regeneration, filtering rate, and on other factors. Deep desiliconization requires the fullest possible removal of cations from the water since the presence of cations gives rise to the appearance of counterions which suppress the dissociation of the anion-exchange material. The effect of the pH value of water on the residual concentration of SiO_3^{2-} in water diminishes with increasing basicity of the anion-exchange material.

The specifications of Soviet-made anion-exchange materials are given in Table 12.1. The properties of the anion-exchange material, grade AB-17-8, are close to the following foreign anion exchangers: Amberlite IRA-400 and Dowex I (USA), Zerolit FF (Great Britain), Duolite A-101 (France), Wofatit SBW (GDR), Levatit M-500 (FRG).

Strongly basic anion exchangers absorb large-size anions of organic acids, along with anions of mineral acids. As they penetrate into the narrow pores of anion exchanger grains, the organic substances remain trapped there and thus cannot be fully removed from the anion-exchange material during regeneration. So, they accumulate in the anion-exchange material and reduce its exchange capacity. The so-called macroporous anion-exchange materials are free of this demerit, for they have large homogeneous pores from which the anions of organic substances can be removed. Synthetic anion-exchange materials of this kind are presently available. They are capable of absorbing 70 to 90 per cent of organic substances contained in water that are subsequently removed from the exchange material to a great extent by regeneration.

12.1.3. Water Demineralization

Demineralization of water is the removal of cations and anions of the substances dissolved in it. The water to be demineralized

Table 12.1
Properties of Anion-Exchange Materials [8]

Grade	Grain size, mm	Bulk mass, t/m^3		Exchange capacity, g-equiv/m^3			Swelling coefficient, %	Moisture content of commercial material, %
		commercial	swollen in water	for SO_4^{2-}	for Cl^-	for SiO_3^{2-}		
ЭДЭ-10П	0.4-1.6	0.6-0.64	0.96	1200	800	—	2.9	15
АН-31	0.4-2.0**	0.72-0.75	0.8	850*	—	—	2.1	15
АВ-17-8	0.3-1.2**	0.72	0.74	—	—	400	2.2	50-60

* For mixture of H_2SO_4 and HCl.
** For swollen material.

usually undergoes preliminary treatment. The water is first passed through hydrogen cation-exchange units for removal of cations, then through anion-exchange units which absorb anions. With removal of ions from the water, its resistivity ρ, Ω cm, increases (i.e. its conductivity $\varkappa$, Ω^{-1} cm^{-1}, decreases).

Deeply demineralized water has $\rho = (5 \text{ to } 10) \times 10^6 \Omega$ cm or $\varkappa = (0.1 \text{ to } 0.2) \times 10^{-6} \Omega^{-1}$ cm^{-1}. The unit of conductivity equal to $1 \times 10^{-6} \Omega^{-1}$ cm^{-1} is called the microsimens per centimeter. Hence, $\varkappa = 0.1$-0.2 μS/cm. The conductivity of partially demineralized water is over 1 μS/cm. Modern demineralizing plants serving boiler-turbine units (see Sec. 12.4) produce condensate with $\varkappa = 0.1$ to 0.15 μS/cm. When ρ is known, the approximate salt content of demineralized water, taken as NaCl, mg/kg, can be determined by the formula

$$C_{291\,K} = \frac{0.54 \times 10^6}{\rho} = \frac{0.54}{\rho'} \tag{12.3}$$

where ρ' is resistivity, MΩ.

Water can be demineralized by chemical (ion-exchange), thermal, electrodialytic, hyperfiltering (reversed osmosis), magnetic, and other methods. The first method involves the expenditure of great amounts of chemicals, a considerable fraction of which is discharged with waste water into rivers and other water bodies. With this method used, it is difficult to fill the requirements for environmental control and the prevention of contamination of natural waters. That is why other methods that permit demineralization of water with a minimum consumption of reagents attract presently the attention of scientists and engineers. These methods are being intensively developed and perfected, and considerable achievements have been made in this field.

12.2. Water Demineralizing Plants

In the ion-exchange demineralization method used, water passes through a number of stages, each of which serves a certain purpose. A series of stages arranged in the required sequence is referred to as a demineralizing system.

If initial water comes from surface sources, it is first directed to pretreatment facilities that include clarifiers and mechanical filters for removal of coarse-dispersed and colloidal impurities and organic substances.

The clarified water is then treated in hydrogen cation-exchange units of the first (H_1), second (H_2), and sometimes of the third (H_3) stages, where all cations (Ca^{2+}, Mg^{2+}, Na^+, NH_4^+ and others) are removed, and further in anion-exchange units of the first (A_1), second (A_2) and third (A_3) stages to remove all strongly basic anions (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-) and weakly basic anions ($HSiO_3^-$, HCO_3^-). The hydrogen cation- and anion-exchange units, H_3 and A_3, are often replaced by a mixed-bed cation- and anion-exchange unit. The units H_1 are usually charged with sulphonated coal, grade CK-1; the units H_2 with the cation-exchange material, grade KУ-2; the units A_1 with the weakly basic anion-exchange material, grade AB-31; and the units A_2 and A_3 with the anion-exchange material, grade AB-17. Low mineralized waters are also treated in units H_2 charged with the CK-1 cation-exchange material.
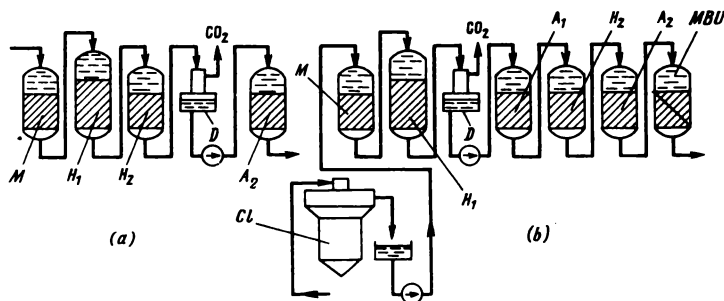
Fig. 12.1. Demineralizing plants

(a) partial demineralization; (b) full demineralization

The number of treatment stages in a demineralizing plant depends on the degree of water demineralization. Figure 12.1 illustrates two demineralizing systems intended for partial and deep demineralization. The first is operated at electric power stations fitted with high- and super-high pressure drum-type boiler units. The second is basically used for modern electric power stations fitted with supercritical-pressure once-through boiler units each operated in set with a turbine.

Using the above notations for exchange units of different stages, the demineralizing systems depicted in Fig. 12.1 can be presented as

follows: the system in Fig. 12.1a as $M — H_1 — H_2 — D — A_2$; the system in Fig. 12.1b as $Cl—M—H_1—D—A_1—H_2—A_2—MBV$, where D denotes a decarbonation tank where CO_2 is removed, and Cl stands for a clarifier.

Other demineralizing systems are also used. For instance, a system of partial demineralization can include the following units: $H_1' — H_1'' — D — A_1$; $H_1' — H_1'' — H_2 — D — A_1$. The decarbonation tank may be installed downstream of the exchange units H_1 or A_1. By suitably changing the order in which the exchange units and the decarbonation tank stand in this "chain", one can devise various demineralizing systems to be used for treatment of natural waters differing in quality. But all of them will be similar to the demineralizing systems shown in Fig. 12.1.

In a water demineralizing system, the greatest ion-exchange load is carried by units H_1 and A_1, i.e. by first-stage units. In order to reduce the breakthrough of cations and also to cut down the consumption of chemicals, two first-stage units are often installed in pairs, one unit after another ($H_1' — H_1''$) as shown in Fig. 12.2. The
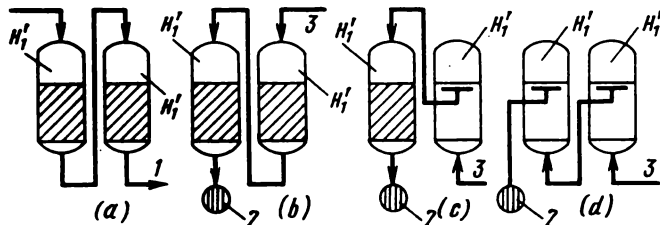
Fig. 12.2. Operating scheme and regeneration of twin units

1 — to feedwater line; *2* — drain; *3* — reagent solution

principle of operation of this pair of units is given in Fig. 12.2a and possible regeneration layouts such as a downflow, a mixed, and a counterflow regeneration layout are illustrated in Fig. 12.2b, c and d, respectively. A similar pair of units is also used as a first-stage anion-exchange demineralizer ($A_1' — A_1''$).

Regeneration of paired units even by the scheme shown in Fig. 12.2b effects a considerable saving of reagents and improves the performance of the H_1'' demineralizing units. The sequence of

regeneration shown in Fig. 12.2c and d materially enhances the operating capacity of the demineralizing equipment. For the depth of regeneration of the bed in unit H_1'' (or A_1'') to be preserved, the unit should be rinsed with the filtrate H_1', A_1', or with partially demineralized water. Paired units are usually employed to treat water with high ion concentration ($\geqslant$ 4 or 5 mg-equiv/l).

The number of first-stage units and their diameter must be so chosen as to carry out not more than three regenerations and not less than one regeneration daily. Attempts should be made to keep in operation no more than four units of this type.

It should be noted that counterflow regeneration carried out as depicted in Fig. 12.2c and d is not sufficiently effective due to unreliable squeezing of the ion-exchange bed. As a result the regenerant is not distributed uniformly over the entire volume of the bed, which impairs regeneration efficiency. Therefore, instead of the paired conventional units, it is expedient to employ special counterflow ion-exchange softeners described above (see Fig. 10.17), which permit a reduction in the specific consumption of regenerants to 1.2 to 1.5 g-equiv/g-equiv.

12.3. Equipment of Demineralizing Plants

12.3.1. Demineralizing Units

Demineralizing plants incorporate conventional ion-exchange softeners described above. Soviet industry produces first-stage ion-exchange units of a greater height, capable of accommodating an ion-exchange bed 2.0 to 2.5 m high. These units are usually operated with a filtering rate of not over 20 m/h, depending on the quality of the water being treated, as seen from formula (10.14). Units of the second and third stages that carry by far a lower ion-exchange load are made smaller in height and designed for an ion-exchange layer 1.5 m thick. The admissible filtering rate for H_2 units is 40 to 50 m/h, for A_2 units it is 20 to 30, and for A_1 units (with an AH-31 type ion-exchanger) below 20 m/h.

The mixed-bed units used only in ion-exchange demineralizing systems are of special design and purpose. These units are charged with a mixture of the KУ-2 type cation-exchanger and AB-17 type anion-exchanger. The action of this mixed bed comes to the following. As evident from formula (10.16), the breakthrough of ions

being removed decreases as their concentration S in the water under treatment falls off. That is why to ensure a more complete removal of ions, use is made of the ion-exchange demineralizing system $H_1 - A_1 - H_2 - A_2 - H_3 - A_3$, in which the water flowing into each subsequent demineralizing unit has a considerably smaller ion concentration. To decrease the ion concentration in the demineralized water to a minimum, it would be more profitable to employ longer demineralizing chains, such as $H_1 - A_1 - H_2 - A_2 - ... - H_{n-1} - A_{n-1} - H_n - A_n$. Chains of this kind are realized in the mixed-bed unit. Here, in the well blended mixture, grains of the КУ-2 type material are in contact with grains of the AB-17 material and form long chains $H - A$ that contribute to deep demineralization of the water mixed-bed cation- and anion-exchange units give filtrate with a conductivity of 0.1 μS/cm or less.

Shown in Fig. 12.3a is the scheme of a mixed-bed unit (MBU) with internal regeneration, and in Fig. 12.3b the scheme of a mixed-bed unit with external regeneration. Filters-regenerators for
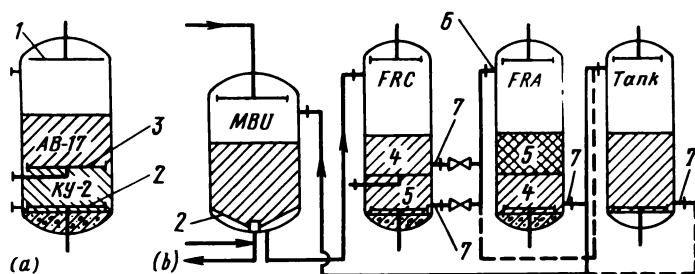
Fig. 12.3. Mixed-bed unit with internal and external regeneration

cation-exchange materials (FRC), for anion-exchange materials (FRA), and the tank for a mixed-bed unit with internal regeneration are mostly used in conventional demineralizing plants, and mixed-bed units requiring external regeneration find application in turbine-condensate demineralizing plants.

A mixed-bed unit has three underdrain-distributing systems: upper (1), lower (2) and middle (3). The last plays an important part in the operation of the unit; it is arranged at such a height from the lower underdrain system that the interface between the КУ-2 cation

exchanger and AB-17 anion exchanger passes along its axis. In accordance with the density of grains of the ion-exchange materials, the cation exchanger is arranged at the bottom and the anion-exchanger on top of it. After the two ion-exchange materials intermix, the interface vanishes and a homogeneous filtering bed forms. The water is passed through the bed in downflow at a rate of 50 to 100 m/h.

Higher filtering rates may cause failure of the middle underdrain system. External regeneration, which is widely applied in industry, obviates these rate-of-flow limitations. By this method, it is necessary to withdraw the exhausted ion-exchange materials from the mixed-bed unit and charge into the FRC for their separation into anion-exchange bed 4 and cation-exchange bed 5. Then, one may proceed in two ways, either regenerate the two exchange materials in the FRC and charge them into the FRA or load the anion-exchange material into the FRA and regenerate the two exchange materials separately. The latter variant reduces to a minimum the regeneration of the KУ-2 exchanger with alkali and the AB-17 exchanger with acid. After separate regeneration is over, the cation-exchange material is loaded into the regenerator FRA. A third vessel (a tank) may also be used where the ion-exchange materials can be mixed after separate regeneration and left in storage for future usage (see the dotted line). After taking out of service the next MBU, the exhausted ion exchangers are removed from it and charged into the FRC and the regenerated mixed ion exchangers are delivered from the tank into the MBU. On completing the check mixing of the ion-exchange materials, the MBU is put into operation, and the discharged ion-exchanger materials are meanwhile regenerated as described above.

Loading and unloading of ion-exchange materials are carried out hydraulically. For this, the demineralizing units and regenerating facilities have special charging (6) and discharging (7) unions, interconnected by piping in the manner as shown in Fig. 12.3. If it is required to discharge the ion-exchange materials from the MBU and charge them into the FRC, water is delivered into the MBU through distributing device 2 to build up a pressure of 0.15 to 0.2 MPa. Then, the valve is opened on the line running to union 6 of the FRC so that the mixture of water and ion-exchange materials can "overflow" into the FRC, from which excess water is removed through the bottom drain. If the system is fitted with suitable piping, the ion-exchanger materials can be removed from

any of the mixed-bed units and charged into the FRC or another vessel. According to design standards, demineralizing plants for turbine condensate are to be furnished with three regenerators for four supercritical-pressure boiler-turbine units rated up to 500 MW. Regenerators are usually made smaller in diameter than mixed-bed units in order that they can have a higher ion-exchanger bed than mixed-bed units. As the latter operate without the middle under-drain system, they permit higher filtering rates, up to 100 m/h and above.

12.4. Demineralizing Plants for Boiler-Turbine Units

The concentration of impurities in the water circulating in the closed circuit (see Sec. 0.2) of a boiler-turbine unit increases gradually. A fraction of the impurities forms in the circuit proper and the other fraction penetrates into the circuit from the outside. The impurities that form in the circuit are mainly the products of corrosion of structural materials, such as Fe_2O_3, Fe_3O_4, CuO, ZnO and others, which are present in the water in a fine-dispersed phase, i.e. as small particles, equal to or less than 0.5 to 1.0 μm in size. The substances penetrating from the outside are found to be either in a dissolved or in a colloidal form. They get into the closed circuit with the cooling water through the leaks in the turbine condenser, with the demineralized water used as makeup for steam and condensate losses, and with the solutions of reagents (NH_3, N_2H_4) if they are prepared with the use of insufficiently treated water.

To maintain the concentration of dispersed and ionic impurities in feedwater for supercritical-pressure once-through boiler units at the prescribed level, the impurities must be removed from the circuit of a boiler-turbine unit. Such removal is ensured by a special demineralizing plant serving each boiler-turbine unit.

In accordance with the nature of the impurities being removed, this plant includes two groups of filters and demineralizing units: mechanical filters for removal of dispersed impurities and mixed-bed demineralizing units. The need for mixed-bed units in a demineralizing system serving a boiler-turbine unit is universally recognized. As to mechanical filters, one can use any alternative variant suited for the purpose. Suspended substances, mainly corrosion products, can be removed by ion-exchange and cellulose

tubular-element precoat-type filters, sulphonated-coal filters, and electromagnetic filters.

The cellulose tubular-element precoat-type filters have a high unit capacity ($\geqslant 500$ m^3/h) and ensure reliable treatment of water. But the use of these filters involves a complexity of operations needed to restore their operating properties (remove and precoat the cellulose layer), cleaning of the waste waters from the drained cellulose, and the necessity of fitting cellulose traps downstream of the filters. Filters with a sulphonated-coal bed are simpler to maintain and are more reliable in operation. They are conventional mechanical filters with a bed of sulphonated coal 0.8 to 1.0 m high.

Electromagnetic filters can also be used in a demineralizing plant, though they are only able to retain the particles of F_3O_4 (magnetite) leaving other dispersed impurities free to move into a mixed-bed unit. However, corrosion products (F_3O_4) are the main impurity in turbine condensate. That is why the employment of electromagnetic filters in a demineralizing plant, instead of sulphonated-coal mechanical filters, is justified.

What distinguishes sulphonated-coal filters from tubular-element precoat-type and electromagnetic filters is the ability to remove ammonia (NH_4^+ ions) from water owing to their regeneration by acids. Ammonia is introduced into the feedwater at district power stations to maintain the pH value at a required level. This prolongs materially the softening run of a mixed-bed unit between regenerations since the ion-exchange capacity of the KУ-2 type material is exhausted by ammonium. In spite of this, at some district power stations, sulphonated-coal mechanical filters are not regenerated, but only backwashed periodically with condensate to remove the trapped impurities and reduce the pressure drop through the filtering bed. At some district power stations the bed of these units is backwashed only during repairs of boiler-turbine units. Instead of rinsing, the filter is drained off 2 or 3 times annually, and the first layer of the cation-exchange material, about 20 to 30 mm thick, is removed because this layer contains the greatest part of the entrapped impurities which cause resistance to water flow.

Practical experience shows that normal deferrization of condensate in a regenerated sulphonated-coal unit of a demineralizing plant is started one to three days after the unit is put into service. This time interval is probably required for the formation in the sulphonated-coal bed of a film of corrosion

products that is responsible for demineralization. That is why, at district power stations where sulphonated-coal units are rarely washed or cleaned of the entrapped impurities manually, condensate is freed of iron oxides to a higher extent (50 to 60 per cent) than at power stations where the sulphonated-coal filters are regenerated periodically (40 to 50 per cent). Optimal operating conditions for sulphonated-coal units should be determined at each district power station, allowing for local conditions.

Estimating the above mentioned mechanical filters in respect to the degree of condensate deferrization, it should be noted that all of them can ensure a 40 to 50 per cent demineralization of condensate containing 8 to 12 μg/kg of Fe. The degree of demineralization rises with the initial concentration of Fe.

In the past few years the tendency has been to operate demineralizing plants of boiler-turbine units without mechanical filters. In the USA, about 80 to 90 per cent of newly designed demineralizing plants do not incorporate such filters. At some Soviet district power stations, demineralizing plants also operate without mechanical filters. One could expect a deterioration in the performance of mixed-bed units due to overgrowing of the granular ion-exchange materials with corrosion products, fast increase in the pressure drop through the mixed bed, and thereby a lesser amount of condensate demineralized during the filtering run. Nothing of the kind happens, however, and demineralizing plants operate well. This tendency, leading to simpler and less costly demineralizing plants, is believed to be substantiated and expected to be followed in the future.

It should be mentioned, however, that whenever it is decided to lay off the installed sulphonated-coal mechanical filters or to operate the plant without installing new filters, it is necessary to take measures that would ensure a minimum concentration of iron ($\leqslant$ 8-10 μg/kg) and CO_2 in the water-condensate circuit of a boiler-turbine unit under steady-state operating conditions. High concentrations of Fe and CO_2 and slow transfer of a boiler-turbine unit to normal duty during lighting-up can result in deteriorated performance of a demineralizing plant in the absence of mechanical filters. The penetration of large amounts of carbon dioxide into the water-condensate circuit of a boiler-turbine unit requires a greater dose of NH_3 to be introduced into the feedwater to maintain a preset pH value, and this leads to a rapid exhaustion of the exchange capacity of mixed-bed units.

12.5. Attendance •
of Ion-Exchange Demineralizing Plants

The way in which the component units of a demineralizing plant are attended does not differ from that practiced in operating cation-exchange softeners described above. The operation of cation-exchange and anion-exchange units of demineralizing plants includes two periods, referred to as runs: the filtering (or softening) run, in the course of which water is treated in the unit, and the regeneration run, during which the exchange capacity of the unit is restored. The amount of effluent water is determined by the filtering rate (see Sec. 12.2). This parameter is usually selected by the designers of the unit, but it depends on a number of other quantities [(see Sec. 10.3, formula (10.14)] and cannot be taken arbitrarily. The lower the filtering rate, the smaller the residual concentration of ions in the filtrate and the greater the exchange capacity, which is of rather great importance to A_2 and A_3 units. This shows how important it is to find optimal operating conditions for demineralizing units.

As the exchange capacity of first-stage units H_1 becomes exhausted, breakthrough of sodium sets in and, consequently, the acidity of the filtrate decreases. As the acidity drops by 0.5-1.0 mg-equiv/kg, H_1 units are shut down for regeneration. The exhaustion of first-stage units A_1 is indicated by the breakthrough of anions, Cl^-, which leads to the yield of acid filtrate. When the concentration of Cl^- rises to 3-5 mg/kg and the filtrate appears to be weakly acid, the A_1 unit is laid up for regeneration.

The requirements on the water after treatment in the H_2 and A_2 units can vary, depending on the ion-exchange demineralizing system and demineralized-water consumers. That is why the quality standards for the filtrate from the demineralizing units must be determined when setting up the plant or they must be preset by designers. The H_3 and A_3 units are terminal units in the demineralizing system; they are laid up for regeneration when filtrate quality parameters become close to the maximum admissible standard values prescribed by regulations.

Approximate operating parameters for regeneration of ion-exchange units are given in Table 12.2.

The regeneration process for these units differs little from that described above (see Sec. 10.3). It comprises three main operations, namely, backwashing the ion-exchange bed; passing through the bed a reagent solution at a preset rate of flow, and rinsing the ion-exchange bed to remove regeneration products. Backwashing is

Table 12.2

Operating Parameters for Regeneration of Demineralizing Units

Operation	Units					
	$H_1(H_1'-H_1'')$	H_2	H_3	A_1	A_2	A_3
Shutting down for regeneration	$Ac_{tr} \le Ac_{iw}$-0.5; $H_s > 200$	Determined during setting-up	$C_{Na} > 20\ \mu g/l$	$C_{Cl^-} = 3$-5 mg/l; Ac_{tr}-weak	When concentration of SiO_3^{2-} increases	Similar to A_2
Backwashing	$v_b = 1.4$-16 for KY-2 and KY-1; 16-18 for CK-1; $t_b = 10$-15	Similar to H_1	Similar to H_1	$v_b = 13$-14; $t_b = 20$-30	$v_b = 12$-14; $t_b \approx 10$-15	Same
Regeneration	$v_r = 10$; $C_r < 2\%$ H_2SO_4	$v_r = 10$; $C_r = 2$-4% H_2SO_4	$v_r = 10$; $C_r = 2$-4% H_2SO_4	$v_r = 4$-5; $C_r = 2$-4% NaOH	$v_r = 4$-5; $C_r = 3.5$-4.5% NaOH	Same
Rinsing	$v_{rin} = 10$ to the end of rinsing; $Ac_{tr} = Ac_{iw} + 1$; $H_t \le 50$	$v_{rin} = 10$ to the end of rinsing; $Ac_{tr} \le 0.3$; $H_t \le 3$	$v_r = 10$ to the end of $C_{Na} \le 20\ \mu g/l$; $H_t < 1$	$v_{rin} = 4$-5; $t_{rin} = 40$-60; $v_{rin} = 10$-12; to $C_{Cl^-} = 3$-5 mg/l; $A_{tr} \le 10$	$v_{rin} = 4$-5; $t_{rin} = 40$-50; $v_{rin} = 10$ to the end of rinsing	$v_{rin} = 4$-5; $t_{rin} = 40$-50; $v_{rin} = 10$ to the end of rinsing; $C_{SiO_2} \le 20\ \mu g/l$; $C_{Na} \le 20\ \mu g/l$; $H_t < 0.3$

Note. Ac_{tr}, Ac_{iw} = acidity of treated and initial water, respectively, mg-equiv/kg; v_b, v_r, v_{rin} = rate of liquid flow during backwashing, regeneration and rinsing, m/h; H_t = hardness of treated water, µg-equiv/kg; t_b, t_{rin} = backwashing and rinsing time, min; C_r = concentration of regenerant solution, %; A_{tr} = alkalinity of treated water, µg-equiv/kg.

accomplished by upflowing water. Although the flow rates of backwash water are usually known and preset, this operation must be carried out without the entrainment by the water of particles of , the ion-exchange bed 0.3 mm or more in size; such carry-over of particles can be observed even at standard rates of water flow. The carry-over phenomenon is usually observed when local high-velocity streams of backwash water appear at spots where the ion-exchange material is loosely packed.

Regeneration with a dissolved reagent and rinsing of the ion-exchange bed are often carried out at the same rate of flow. Hydrogen cation-exchange units are regenerated and rinsed with a rate of 10 m/h. First, anion-exchange units are regenerated and rinsed for about 40 to 50 min at a rate of 4 or 5 m/h, then the flow rate is increased to 10-12 m/h. In delivering the regenerant solution into a unit, the pressure inside it must be kept 0.05 MPa below the pressure in the units in service to prevent the penetration of the dissolved regenerant into them. Such penetration can also be prevented by fitting on the regenerant line, upstream of each unit, two stop valves with a drain pipe between them. This permits checking the stop fittings for air-tightness.

The demineralization process is associated with the consumption of great amounts of reagents and water required inside the plant. That is why the rinsing water (from second- and third-stage hydrogen- and cation-exchange units and from mixed-bed units) must be repeatedly used for backwashing, preparation of regenerant solutions and for rinsing of units to remove regeneration products. Rinsing must be done with water containing an insignificant amount of the ions which can be trapped in the unit being rinsed. Attempts must be made to exclude exhaustion of the bottom part of the ion-exchange bed exposed to the water leaving the unit. This is of particular importance to first- and second-stage demineralizing units.

Anion-exchange materials, especially strongly basic ones, also retain the organic substances present in the treated water. These substances are sorbed as ions or trapped on the surface and in the pores of the anion-exchange grains. Large molecules of organic substances penetrating into these pores cannot be displaced from them during the short regeneration time and thus cause "poisoning" of the ion-exchange material and a considerable decrease in its exchange capacity.

This has necessitated the development and application of

a number of techniques. Since organic substances cannot be fully removed by conventional pretreatment, demineralizing plants have been fitted with sorption filters charged with activated carbon and mounted upstream of anion-exchange units. Subsequently, in the USSR and in other countries, synthetic anion-exchange materials have been developed: they are noted for relatively large pores (macroporous materials) and uniform porosity (isoporous materials). Macroporous anion-exchange materials are capable of reversible absorption of organic substances. Nevertheless, much attention should be given to the methods that enable most complete removal of organic substances from water upstream of the anion-exchange units.

Review Questions

1. What distinguishes the anion-exchange process from the cation-exchange process?

2. What reaction (pH) of water is favourable for the anion-exchange process?

3. What is the essence of the water demineralization process?

4. Why is it necessary to have a decarbonation tank in the water demineralizing system?

5. What is the characteristic feature of the ion-exchange process in mixed-bed units?

6. What are the advantages of external regeneration?

Bibliography

1. **Akolzin, P.A.** *Preduprezhdenie korrozii metalla parovykh kotlov* (Prevention of Metal Corrosion in Boilers), M., Energiya, 1975.
2. **Akolzin, P.A., Margulova, T.Kh., Martynova, O.I.** *Vodny rezhim paroturbinnykh blokov sverkhkriticheskikh parametrov* (Water Control for Supercritical-Pressure Boiler-Turbine Units), M., Energiya, 1972.
3. **Apeltsin, I.E., Klyachko, V.A.** *Opresnenie vody* (Water Desalting), Izdatelstvo Literatury po Stroitelstvu, 1968.
4. **Belan, F.I., Sytotskiy, G.P.** *Vodopodgotovka promyshlennykh kotelnykh* (Water Treatment in Industrial Boiler Houses), M., Energiya, 1969.
5. **Vikhrev, V.F., Shkrob, M.S.** *Vodopodgotovka* (Water Treatment), M., Energiya, 1973.
6. **Gurvich, S.M., Kostrikin, Yu.M.** *Operator vodopodgotovki* (Operator of Water-Treatment Plant), M., Energiya, 1974.
7. **Margulova, T. Kh.** *Primenenie kompleksonov v energetike* (The Use of Complexing Agents in Power Generation), M., Energiya, 1973.
8. **Spravochnik** khimika-energetika (Chemical-Power Engineer's Handbook), M., Energiya, 1972.
9. **Styrikovich, M.A., Martynova, O.I., Miropolskiy, Z.L.** *Protsessy generatsii para na elektrostantsiyakh* (Steam Generation at Electric Power Stations), M., Energiya, 1969.
10. **Subbotina, N.P.** *Vodny rezhim i khimicheskiy kontrol na teplovykh elektrostantsiyakh* (Water Control and Cycle Chemistry at Heat Electric Power Plants), M., Energiya, 1974.
11. **Khimicheskie** ochistki teploenergeticheskogo oborudovaniya (Chemical Cleaning of Power Generating Equipment), edited by Margulova, T.Kh., M., Energiya, 1969.

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